













# METALLURGICAL ANALYSIS

*By*

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## PREFACE TO THE FIRST EDITION.

The book is based on the experience gained in the Chemical Laboratory of the Tata Iron and Steel Works, Jamshedpur, from 1918 to 1923, and in the Department of Mining and Metallurgy of the Benares Hindu University, since 1923, when the Department was first established. It will be seen that the author has been in no hurry to rush to print and add yet another to the fair number of books on the subject of 'Metallurgical Analysis'. Many a student has expressed his difficulty in following those available in that they either assume too much on his part and omit important details, or give too many details. The student is at sea when called upon to make a determination, for want of sufficient details or he is lost in a multitude of details, without the ability to state precisely the principle on which a particular determination or a separation is based. The author believes that he has tried to set forth clearly both the principles of each determination, and the procedure.

Though the book has been written primarily to meet the needs of the students preparing for the B. Sc. degree Examinations in Mining and Metallurgy of the Benares Hindu University, it is hoped that it will be serviceable to those engaged as chemists and metallurgists in railway workshops and to those chemists employed in the control laboratories of the fair number of steel works in this country making steel by the electric furnace process.

No apology is needed for including methods for the

testing of lubricants, as chemists in a steel works and in railway workshops are often called upon to report on the qualities of lubricants.

The establishment of aluminium industry in this country is almost an accomplished fact and methods for a few estimations in connection with the analysis of the raw materials and the finished products of this industry have been included.

In a branch of analysis which has been growing from the year 1830, when steel-making by modern methods may be said to have begun, it is not possible to write anything original and the author is specially indebted to the following works of reference :—

1. Analytical Chemistry, Volume II, by F. P. Treadwell and W. T. Hall,
2. The Methods of the Chemists of the United States Steel Corporation,
3. Applied Inorganic Analysis by W. F. Hillebrand and G. E. F. Lundell,
4. The British Aluminium Co's publication entitled 'Analysis of Aluminium and Its Alloys'.
5. Select Methods of Metallurgical Analysis by W. A. Naish and J. E. Clennell and
6. The B. D. H. Book of SPOT TESTS, 1941 Edition.

The author's grateful thanks are due to the following firms, organisations and gentlemen for permission to reproduce illustrations from their catalogues and publications and for the loan of blocks :—

Messrs. Griffin and Tatlock, Ltd., London,  
 „ Gallenkamp and Co., Ltd., „  
 The American Society for Testing Materials, Philadelphia.

The Indian Stores Dept., Government of India, His Majesty's Stationery Office, London,

The Balance Works, Benares,

Nand Kishore and Brothers, Benares  
and Prof. M. L. Schroff, Head of the Department of Pharmaceutics, Benares Hindu University.

The co-operation of the following firms by presenting to the Department specimens of raw materials, intermediate and finished products has been invaluable and the author's thanks are due to them :—

1. The Tata Iron and Steel Co., Ltd.,
2. The Indian Copper Corporation, Ltd.,
3. The Mysore Iron Works.
4. The Oorgaum Mines, Ltd., and
5. The Burma Corporation, Ltd.

Thanks are due to Dr. Daya Swarup, Head of the Department of Mining and Metallurgy, for permission to reproduce drawings of furnaces in the Fire-Assay Laboratory and to publish analytical data regarding materials analysed in the Department.

Thanks are also due to my colleague, Mr. U. V. Bhat, for help in correcting the proofs.

Suggestions for the improvement of the book will be gratefully accepted.

Benares Hindu University,

V. G. Iyer

., February 1943.



## PREFACE TO THE SECOND EDITION.

In response to suggestions from those fellow-workers in charge of the control laboratories of large centres of production of metals who reviewed the first edition of this book and from those who use it regularly, the subject-matter has been rearranged and division into 'Chapters' made. It is hoped that this procedure will facilitate ready reference to sections or exercises in which one is interested. Passing mention may be made of the following additions :—Separations involving the use of ethyl ether, determination of aluminium, arsenic, titanium and nitrogen in Steel and of sulphur in Steel by the combustion-titration method.

The author's grateful thanks are due to the Council of the Iron and Steel Institute for their permission to reproduce from their Journal illustrations of the apparatus used for the determination referred to last, namely, sulphur in Steel.

Owing to the continuance of war-time controls even after the cessation of hostilities, making it difficult to import apparatus involving the application of advances in Physics to the speeding up of the processes of analysis, like the Spekker Absorptiometer, the Quartz Spectrograph, the Carbometer, etc., the author has been obliged to rest content with the rearrangement and description of those methods only of which he has had long experience. He hopes that this present edition with all its imperfections, will be accorded the same kind reception as the first.

Benares Hindu University, }  
July 1947-

V. G. Iyer.

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## CHAPTER I

### THE BALANCE, ITS ADJUSTMENT AND USE.

The most essential requisites of a balance serviceable for purposes of quantitative analysis are that it must be accurate and sensitive. It fulfils the first condition if the two arms of the lever are of equal length, if the point of support, lies above the centre of gravity, and if the fulcrum, which is a knife edge, and the knife edges from which the pans are suspended lie in the same plane and are parallel to one another.

The sensitiveness of a balance may be expressed by the equation:

$$\tan \alpha = \frac{l}{d}$$

where  $\alpha$  = angle of swing of the pointer from its position of rest,  $p$  = the small difference in weight between the loads on the two pans,

$l$  = the length of the beam,

$q$  = the weight of the beam,

and  $d$  = the distance between the point of support and the centre of gravity.

All good balances are provided with a device by means of which  $d$  may be adjusted. This consists of a metallic bob known as the moment of inertia bob which can be moved up and down a screw upright fixed to the middle of the beam. By increasing  $d$  by means of this device, the sensitiveness is diminished whereas by decreasing  $d$ , it is increased. This last operation increases the time of swing so that the time taken to make a weighing is correspondingly increased. To enable the weighing operations to be carried out

more expeditiously without any impairment of accuracy, Lord Rayleigh loaded the pointer with a sphere which can be slid up or down its entire length. The turning points of the pointer are observed through a magnifying glass. The greater accuracy in reading compensates for the somewhat decreased sensitiveness.

In the Laboratory of this College, we have balances of both types: one type where  $d$  can be varied by the movement of the moment of inertia bob, and the other type where Lord Rayleigh's principle of loading the pointer is incorporated.

### Use of the Balance.

See that the feet of the balance lie in the horizontal plane. This is secured by means of a spirit-level. Some types of balance rest on four legs each of which can be raised or lowered; some have three legs each of which can also be raised or lowered while others have three legs of which only two are adjustable. The first type is levelled by placing the spirit-level along a line joining any two legs and adjusting these until the air-bubble comes to the middle of the level-scale. Next, it is placed in a position at right angles to the previous position, the remaining screws being now adjusted.

The second type is adjusted as follows :—

Place the level approximately along a line joining any two screws and adjust till the air bubble comes to the middle. Next place the level at right angles to the previous position and adjust the remaining screw until the bubble comes to the middle.

The adjustment for the third type is as follows :— Place the level along a line joining one screw-leg with the one without screw and adjust as described above. Next place along a line joining the other

screw-leg with the one without screw and again adjust as described above. The balances in use in the College are of the first and last types.

### **Weighing by the Method of Oscillation.**

Determine the resting point of the balance (Fig. 1 a) at Zero-load. To do this, release the beam gently by

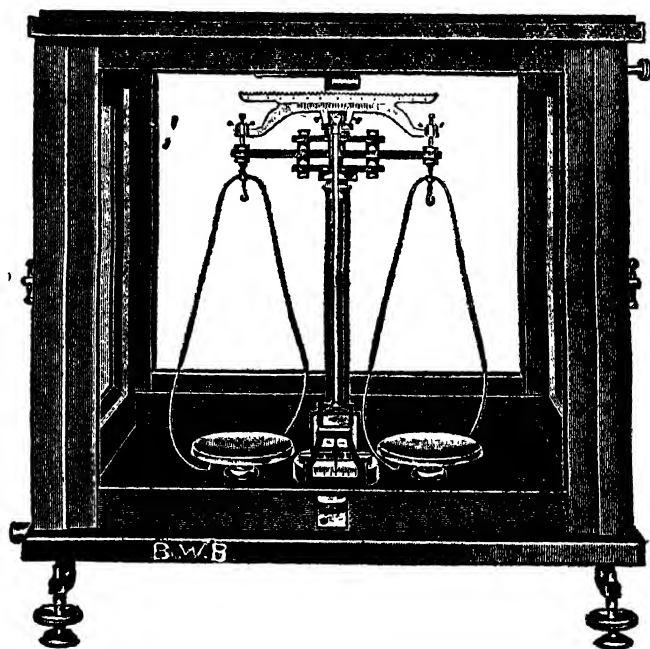


Fig. 1 a

turning the handle in front or at the side and blow on one of the pans gently. Ignore the readings of the pointer corresponding to the first two swings. This is for the purpose of avoiding any error due to hard, instead of gentle, blowing on one of the pans. Note the extreme divisions on the scale over which the pointer moves. Take the extreme left graduation as Zero and note the readings corresponding to the swing of the pointer on the left and on the right. Do this 3 or 4 times taking the consecutive readings. Enter as follows :—



	<i>Left.</i>	<i>Right.</i>
	4	20
	4.5	19
	5	19
	<u>5.5</u>	<u>        </u>
Total	19	58
Mean	4.75	19.3

Sum of the Means = 24.05

Average of the sum of the Means =  $\frac{24.0}{2} = 12.0$  "

Then put the body to be weighed on the left hand pan and the weights on the right hand pan. Suppose a point of equilibrium is nearly attained with a weight of 23.404 gms. In this case find out the resting-point as described above. Thus

	<i>Left.</i>	<i>Right.</i>
	5	21
	6	20
	6	
Total	17	41
Mean	5.6	20.5

Sum of the Means is  $5.6 + 20.5 = 26.1$

Average of the Sum of the Means =  $\frac{26.1}{2} = 13.05$

Increase the weight to 23.405 gms. and find out the resting-point as above. Let it be 11.5. The addition of 1 mgm. has produced a shift of 1.5 divisions in the resting-point. To produce a shift of 1 division,  $\frac{2}{3}$  or .66 mgm. must be added. Thus the weight of the body is 23.4047 gms. . This method of weighing is known as the method of weighing by oscillation.

.0007 gm. is the sensibility of the balance at a load of 20.25 gms., this being the weight required to shift

the resting-point through one division when the mass weighed is about 20-25 gms. The sensibility of a balance is expressed sometimes also as the number of divisions of shift of the resting-point produced by the addition of 1 mgm. to one of the pans. It is a factor which varies with the load and is different for different balances. Draw up a table of sensibility for loads of

60 gms.  
 20 gms.  
 10 gms.  
 5 gms.  
 and 2 gms.

In recent years balances known as the 'Chainomatic' (Fig. 1b) have been introduced. With these it is possible

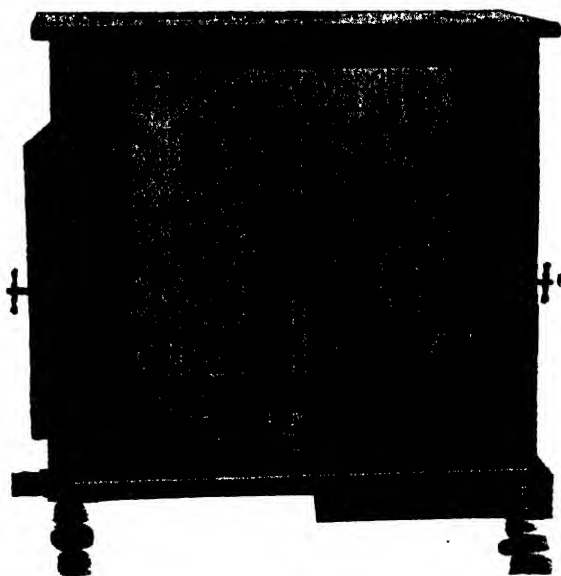


Fig. 1 b

to carry out a weighing operation more expeditiously than formerly, as no fractional weights of less than 0.100 gm. denomination are required and the use

of a rider is dispensed with. A chain made of thin gold wire has one of its ends attached to the beam, the other end being suspended from a hook fixed to a vernier attachment which moves over a vertical scale. The vernier is moved up and down the scale by turning a handle at the side. The effective weight of the chain can be read off on the scale, each scale division corresponding to a mgm. and the position of the vernier scale gives the weight to the tenth of a mgm. .

### **Rules to be observed in using the Balance:—**

(1) Things should not be weighed before they are cooled to the temperature of the balance room.

(2) The beam should be at rest when adding or removing weights.

(3) No chemical should be weighed directly on the pan.

(4) Weights must always be handled with the pair of forceps provided for the purpose.

(5) The adjustments must not be tampered with by a beginner.

**NOTE:—**It is not necessary that the zero at 'no load' should be the middle division of the scale over which the pointer moves. If there are 24 divisions on the scale, the zero at 'no load' may lie at 10 or 15 or anywhere between. Weighings made with the zero at 10 or 15 are as accurate as weighings made with the zero at 12. Hence no time should be lost in always bringing the zero at 'no load' to 12. If the zero lies at 5 or 6, it is necessary to bring it near 12. This is done in some types of balance, by adjusting one of the nuts attached to a threaded pin fixed to the beam very near the points wherefrom the pans are suspended, while in others it is done by a device the principle of which is in effect the same as the one involved in the above

manipulation. This consists in moving in or out the two nuts attached to a straight piece connected at a variable angle to the moment of inertia bob upright. We have both the types in the Laboratory.

### Box of Weights.

Individual weights in one set of a box of weights must not be exchanged with weights in another. A 10 gm. weight in one may be 10 times the weight of the 1 gm. weight in the same box. But this same relation may not obtain in the case of the 10 gm. weight in one and the 1 gm. weight in the other. In calculating the percentage of a constituent from the weight of an ignited precipitate on, say, a 5 gm. sample of a material, we divide the weight obtained by 5 and multiply by 100. While the factor obtained with the same box of weights for the original and the final weighing, may be, say  $\frac{1}{100}$ , with one box of weights for the original weighing and a different box for the final weighing, the factor may be either  $\frac{1}{100}$  or  $\frac{1}{101}$ , thus leading to inaccuracy in results.

The set of weights provided in a box should be tested to see how far they agree among themselves, in the case, say, of units of 0.2 gm., 0.1 gm., 1 gm., 2 gm., 10 gm., 20 gm., etc. and whether the 5 gm. unit equals the units of 2 gm. + 2 gm. + 1 gm., the 50 gm. unit equals the units of 20 gm. + 20 gm. + 10 gm. units and so on. The process of checking the correctness of the units of weights in a box is known as calibration.

The following are the tolerances on weight units allowed by the Bureau of Standards, Washington, U.S.A.—

Denomination.	Tolerance.	Denomination.	Tolerance.
50 gm.	0.3 mgm.	500 mgm.	0.05 mgm.
20 "	0.2 "	200 "	0.05 "
		100 "	0.05 "
10 "	0.15 "	50 "	0.03 "

Denomination.	Tolerance.	Denomination.	Tolerance.
5 „	0.15 „	20 „	0.03 „
2 „	0.10 „	10 „	0.02 „
1 „	0.10 „	5 „	0.02 „

In analytical work for control operations on the processes of manufacture, correction of weights for buoyancy by air is not necessary.

The litre is defined as the volume occupied by a quantity of pure water at 4° C. having a mass of one kilogram. One thousandth part of the litre is designated the millilitre and this term is used in preference to the term the cubic centimetre, the use of which is being discouraged by Scientific Societies. The cubic centimetre is not exactly the one-thousandth part of the litre. 1 ml.= 1.000027 c. cms. Though the difference between the two is not very great, in conformity with the usage now being strongly recommended and adopted, throughout this book the term 'millilitre' is used.

According to the Bureau of Standards, Washington, D. C., the following are the requirements of apparatus, graduated flasks, burettes and pipettes used in volumetric analysis :—

Diameter in millimetres of the tube portion carrying graduation mark	Capacity of flask, millilitres up to and including					
	50	100	200	250	500	1000
Maximum	10	12	13	15	18	20
Minimum	6	8	9	10	12	14

### Tolernaces.

Capacity.	Limit of Error.	Capacity.	Limit of Error.
50 ml.	0.05 ml.	500 ml.	0.15 ml.
100 „	0.08 „	1000 „	0.20 „
200 „	0.10 „	2000 „	0.50 „

## Tolerances in Volumes marked, Burettes and Pipettes.

	Burette	Pipette.
ml.	ml.	ml.
5	0.01	0.02
10	0.02	0.03
20	0.03	0.04
50	0.05	0.08
100	0.10	0.15

### Removal of greasiness or oiliness from measuring vessels.

The inner surface of all measuring vessels, graduated flasks, burettes and pipettes-must be free from greasiness or oiliness. This is made evident by drops of liquid adhering to the surface when such vessels are filled with water or the solution of a substance in water. This oiliness is eliminated by filling the vessels with a warm ( 40° to 50° C. ) mixture of conc  $\text{H}_2\text{SO}_4$  containing 10 gms. of potassium or sodium dichromate per 100 ml. of the acid, letting them stand for 10 to 30 minutes, emptying them out and washing them with tap-water a number of times. The mixture of conc.  $\text{H}_2\text{SO}_4$  and dichromate should not be thrown away. It can be used over and over again and therefore should be kept in the stock-bottle.

### Common operations in the Laboratory with a note on Laboratory apparatus.

**Bending of glass tubing :—**For diameter of tubing up to about 8 mm., make a scratch (about 2 mm.) with a sharp triangular file at the point at which the tube is to be cut. Move the file in one direction only. Do not use it as a saw, as the sharp file edge gets worn out

by such a procedure. Place the two thumbs on the side opposite to the point at which the scratch has been made and give a pulling-apart motion simultaneously with a bending motion. Very often the cut that results is a square cut, without sharp or uneven points. Sometimes sharp edges are to be seen. In either case, rotate the cut ends over a Bunsen flame until the glass softens. This process is sometimes referred to as 'fire-polishing'. To cut tubing of larger size than 8 mm. diameter, one of two procedures may be adopted. Make a scratch as before with a sharp file. Melt the end of a glass rod, drawn out to a point and place the hot bead of glass on the file-scratch mark. Repeat heating the bead and placing it on the scratch mark until a sharp noise is heard and the glass has cracked. Now lead the crack all round the tube by repeatedly heating the glass rod and bringing it to within a few mm. of the crack already started. The crack is led all round by repeating the process a number of times. The glass tubing thus cut may present a neat appearance or it may have sharp edges. It is fire-polished by rotating it in the flame of a blast-lamp.

The flame from this lamp is about  $150^{\circ}$  to  $200^{\circ}$  C. higher than that from a Bunsen burner. The blast of air used in the blast-lamp effects a better mixing of gas and air and therefore a higher temperature results.

After fire-polishing, bending, etc., operations, the articles must be covered with a deposit of soot to allow them to cool slowly. This is accomplished by allowing the luminous flame to play on them. All that is necessary to get a luminous flame is to stop working the foot bellows, when the blast lamp is being used, or to close the air supply by turning suitably the slotted sleeve at the base of the Bunsen burner, when it is being used.

An alternative process of cutting tubes of diameters over 8 mm. is to wrap two strips of filter-paper or blotting paper to a thickness of about  $\frac{1}{4}$ " on either side of the point at which a tube is to be cut and to hold them in position either with gum-paste or to tie them by means of lengths of sewing cord. Wet the strips with water and rotate over a sharp flame of a blast lamp, directing the flame to the gap between the two strips. After a few minutes of heating, the tube will come off in two. The strips are removed when the tube has become cold. Remove the roughness of the cut edges by rotating in a blast lamp flame.

For fitting up a wash-bottle, two pieces of glass-tubing each 3 to 5 mm. bore should be so bent that the two bends form together two right angles. For the purpose of bending glass-tubing, a long length of flame is required. A batwing burner gives such a flame. Rotate the tubing gently as it is being heated, while the two ends are being supported with both the hands between the fingers. This procedure ensures uniform heating all round. When the tube has softened (sagging is the indication), take it off the flame and bend to the desired angle. Cover with a deposit of soot. Allow to cool. When cool wipe off the soot with a duster.

For drawing out into a jet, rotate as before a convenient length of tubing as it is being heated. When it has become soft, take it off the flame and draw out by pulling at both ends. When cold, the drawn out and tapering portion is cut in the middle by making a scratch with a file and breaking. The cut end is fire-polished by holding it in a very small flame for a very short while only. Heating too long will lead to the closing of the hole.

In boring holes in a cork, moisten the borer with



water and bore from the smaller or narrower end. In the case of rubber corks, moisten the borer with a dilute solution ( normal ) of caustic soda.

In fitting up wash bottles, it is a good practice to give a bend to the long tube reaching to the bottom of the wash-bottle, as this procedure makes it possible to use up almost all the water in the bottle before refilling it. A wash-bottle so fitted up is shown in Fig. 2.

Of funnels of different makes, those with a longer stem and a shorter bore stem are to be preferred to those which have a short and large bore stem. The former are more rapid in filtration work. Again ribbed funnels are more rapid than the plain variety.

### **Desiccators :—**

Conc. sulphuric acid is not a very desirable desiccant to be used in desiccators. When carrying these from the laboratory to the Balance Room, the liquid is likely to be splashed on to crucibles, which are being allowed to cool therein. Anhydrous calcium chloride is convenient. It must be changed when it shows signs of having lumped up. Porcelain discs with holes serve as much better crucible supports than perforated Zink discs.

### **Choice of Weight of Material for a Determination.**

Before commencing any analytical work, the question that arises is 'what is the weight of material to be taken ?' In Works' laboratories, the practice is to use what are known as factor weights. The weighing out of such quantities as have been indicated in exercises dealing with the analysis of iron ore, steel, etc., facilitates calculations, very little time being consumed in the process. Either a platinum scoop and a counterpoise of

lead or a copper scoop and a counterpoise of lead are used. The material to be weighed is introduced, by means of the blade of a stainless steel knife, on the scoop and the powder shaken off or tapped off from the blade until the equality of weight of the material to the factor weight is obtained. The accuracy to which the material is to be weighed need not be more accurate than the process of analysis justifies. In the case of the determination of Sulphur in Pig Iron or Steel, weighing to the nearest centigram will do.

### **Choice of type of vessel.**

What is the type of vessel into which the material weighed is to be transferred? For effecting a solution of iron ore, manganese ore, etc., a 50 or 100 ml. wash-bottle shaped flask is desirable. A beaker or evaporating dish would mean a large consumption of acid and time for effecting solution. But in the case of evaporation to dryness followed by baking, a basin or casserole is to be used. Again where a residue insoluble in acids is also required along with the amounts of matter dissolved, a wash-bottle type flask must not be used, as dislodging of the residues sticking to the side, with the help of a 'policeman', is impossible.

Coors, Sillax and SCP brands of porcelain ware, Pyrex, Jena and Vycor brand glass ware are very serviceable; they are heat-resisting and strong. Porcelain crucibles can in many cases be replaced by silica crucibles (Vitreosil). The former cannot be introduced into the hottest parts of a muffle furnace at  $900^{\circ}\text{C}$ . or  $1000^{\circ}\text{C}$ , whereas the latter can be so introduced without fear of their cracking. Being much cheaper than platinum, they are often used in place of the latter except where fusions with  $\text{Na}_2\text{CO}_3$  are involved. Both platinum and silica ware are unserviceable for fusions

with NaOH. Silica crucibles are also unserviceable for igniting precipitates leading to the formation of CuO, PbO, etc. .

To clean silica crucibles which have become stained, fuse in them about 2 to 3 gms. of potassium bisulphate and keep the mass molten for 2-3 minutes. During fusion support on silica triangles. Cool. Wash out with water. Silica tubes (pyrometer sheaths) must not be immersed in molten NaCl.

If employed at temperatures above  $1100^{\circ}\text{C}.$ , the silica vessels devitrify, lose their strength and tend to become brittle. They should not, therefore, be heated above  $1100^{\circ}\text{C}.$  .

Porcelain crucibles should not be used for sulphur determination in coal by the Eschka method. The glaze is attacked and the surface is pitted by the  $\text{Na}_2\text{CO}_3$  entering into the composition of the Eschka mixture.

### **Care of Platinum Apparatus.**

( 1 ) It should not come in contact with aqua regia.

( 2 ) It should not be used in fusions where caustic alkalies are to be employed.

( 3 ) Salts of reducible metals like lead, tin, bismuth, arsenic and should not be heated in it.

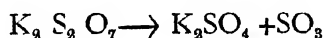
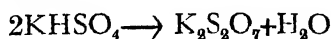
( 4 ) When red-hot, it should be handled with a pair of platinum-tipped or nickel tongs.

( 5 ) It should be supported on a silica, chromium-nickel alloy, or platinum, triangle when fusions are conducted or when precipitates are ignited.

( 6 ) It should not be heated over a smoky flame. Finely divided carbon alloys with platinum and the carbide thus formed readily dissolves in acids. The constancy of weight, which is the most valuable property

of platinum vessels, is affected; besides, loss of a costly material occurs.

( 7 ) To clean a platinum crucible or dish, proceed as follows:—2·3 gms. of sodium or potassium bisulphate are placed in it and slowly heated. First, water is driven off and then fumes of  $\text{SO}_3$  are evolved. These attack the residue which is left in the crucible from a previous experiment, at a temperature of  $300\text{--}900^\circ\text{C}$ . The vessel is then cooled and the residue dissolved off in water. The following reactions take place when potassium or sodium bisulphate is heated.

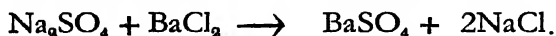


When there is no residue to remove, keep crucible immersed in cold conc.  $\text{HCl}$  for 12 hours and wash with water.

( 8 ) When there is no residue to remove from the crucible and when it is desired to brighten the dull surface, it should be rubbed inside and out with sea-sand moistened with water. Preference to sea-sand is given on account of the roundness of its particles. Sand from other sources has a cutting or scouring action on platinum, which is a soft metal.

**Process of analysis :** The material that has been weighed out is dissolved in a suitable medium and the constituent which is to be determined is thrown down in the form of its most insoluble compound (a precipitate), under carefully controlled conditions of acidity or alkalinity and temperature, by the addition of a precipitant. An excess of the latter should always be provided. If, for example, the amount of sodium sulphate present in a litre of a solution is to be determined, the amount of barium chloride ( precipitant ) which is added should

be in amounts greater than what is needed for the reaction represented by the following equation :—



142 gms. 208·4 gms. 233 gms. 117 gms.

The equation shows that for the precipitation of 142 gms. of sodium sulphate, 208·4 gms. of barium chloride will be required. About 210 or 215 gms. of the latter should be added. In unknown cases, the presence of excess of the precipitant is ensured by the following procedure:—A certain quantity of the precipitant is first added to the solution which is contained, say, in a beaker. The precipitate is allowed to settle, a few millilitres more of the precipitant are added slowly from a pipette along the side of the beaker and the formation of a further quantity of precipitate looked for at the surface of contact of the two solutions. If a precipitate appears, more of the precipitant is added and the precipitate formed is allowed to settle. Again the process of addition of the precipitant is repeated until there is no more formation of a precipitate.

With due regard to the time required for conducting an analysis, the size of vessels, the volume of precipitate to be dealt with, etc., only about a thousandth of each of the quantities indicated by the above equation is employed in practice.

The objects of controlling the acidity or alkalinity of the medium in which a precipitate is thrown down are : (1) the prevention of the co-precipitation of certain other compounds and (2) the formation of the desired precipitate in an easily filterable (i.e.) crystalline, not colloidal, form. It must be remembered that in practice one has to deal not only with cases of precipitation like the simple one referred to above but also with complex mixtures.

A striking example of such a complex mixture is a solution containing the chlorides of arsenic, antimony and tin. By careful adjustment of the amount of acidity ( Hydrochloric acid ), it is possible to throw down completely arsenious sulphide only by passing a current of hydrogen sulphide through the mixed solution. This adjustment is secured by keeping the acidity at, what has been described as the '*pH* value', a certain figure. A solution having a concentration of  $10^{-8}$  gm. of hydrogen ions per litre has a *pH* value of 3 and one having a concentration of  $10^{-4.8612}$  gm. of hydrogen ions per litre has a *pH* value of 4.8612. In other words, the *pH* value of a solution is the logarithm to base 10 of its hydrogen ion concentration prefixed by a negative sign. For each precipitation reaction, there is a certain optimum *pH* value. *pH* values less than 7 indicate that the medium is acid and values greater than 7 that the medium is alkaline. For the precipitation of barium sulphate the *pH* value should be kept at about 1.

The second object for which the regulation of the *pH* value of a solution is controlled is the formation of a precipitate in a crystalline condition. Unless the precipitate is in this form, no filtering medium ( paper or asbestos ) will retain it. A familiar example of matter in colloidal form is arsenious sulphide. When a current of hydrogen sulphide is passed through arsenious acid, the solution is coloured yellow. When this solution is filtered through the closest - textured filter-paper available, it will be found that no particles are retained by the filter paper. If prior to filtration, an electrolyte like hydrochloric acid or sodium chloride or potassium chloride is added and the solution is then filtered, it will be found that the particles of arsenious sulphide are completely retained. The most favourable

electrolyte for each precipitation reaction which is considered in this book is pointed out at the appropriate place. It should be clearly borne in mind that when freeing a precipitate from contaminants by the process of washing with distilled water, there is the danger that with their removal the precipitate may pass into a colloidal form and run through the filter paper, defeating the object of filtration. It is therefore necessary to introduce a suitable electrolyte in the wash water. Potassium nitrate is introduced in the wash water for freeing the precipitate of ammonium phosphomolybdate from nitric acid when it is subsequently dealt with by the alkalimetric titration method.

#### Note on Filtration and Filter Papers:—

The rapidity of chemical analysis is conditioned by the rapidity with which the filtration operation can be performed. Precipitates are either coarse-grained, fine-grained or gelatinous. There is a grade of filter-paper suited for each of these classes of precipitates. The following table is indicative of the brands of make of filter-paper and the precipitates for the filtration of which they are most suited:—

Nature of ppte.	Whatman Brand (English)	Schleicher and Schüll (German)	Delta (German)	Baker Adamson (American)	Munk-tell Swedis Filter-paper
Gelatinous like $\text{Fe}(\text{OH})_3$ , $\text{Al}(\text{OH})_3$ , $\text{SiO}_2$ , $(\text{NH}_4)_3\text{PO}_4$ , $12\text{MoO}_3$ .	31	589 (Black ribbon)	365 (Blue cross)		
Coarsely crystalline like $\text{PbCl}_2$ , $\text{AgCl}$ , $\text{CaCO}_3$ , $\text{PbS}$ , $\text{CuS}$ , $\text{As}_2\text{S}_3$ , $\text{Sb}_2\text{S}_3$ , $\text{ZnS}$ , etc.	30	589 White ribbon)	366 (Brown cross)		
Finely crystalline like $\text{CaC}_2\text{O}_4$ , $\text{BaSO}_4$ , $\text{PbSO}_4$ , $\text{SnO}_2$ , etc.	40, 41 or 42	589 (Blue ribbon)	367 (Green cross)	Quality 'A'.	100

The size of the paper used, ( i. e., its diameter ) does not depend on the volume of the liquid to be filtered but only on the bulk of the ppte. . In case large size filter-papers are used and a determination is to be made on the filtrate, the amount absorbed by the large size paper may be large enough to introduce an error in the determination.

Filter-papers should not be filled to the brim with the liquid to be filtered. They should be filled only to within a quarter of an inch below the edge of the paper. Certain pptes. have the property of creeping to the edge of the paper and if the paper is filled completely, the amount of precipitate creeping up may be lost. Filter-papers should be so chosen that when folded and fitted into the funnels, their edges are 0.25" below the rim.

To avoid loss of filtrate by splashing, the funnel stem should be touching the side of the beaker or flask in which the filtrate is being received or collected.

When ignition of the precipitate with the filter-paper will lead to a reduction reaction by the carbon of the filter-paper as in the case of  $\text{BaSO}_4$ ,  $\text{PbSO}_4$ , etc., one of two courses is open: ( a ) carrying out the ignition at a temp. low enough not to bring about reduction as in the case of  $\text{BaSO}_4$  or ( b ) filtering through a Gooch crucible with asbestos packing as in the case of  $\text{PbSO}_4$ . The danger of reduction is always there when  $\text{PbSO}_4$  is ignited with the paper at temp. low enough to convert the paper into ash. Hence filtration through asbestos is a necessity. Where several determinations of the same kind are to be made, there is considerable saving in time in using the Gooch Filter.

### Devices for Filtration.

To expedite filtration of fine precipitates through paper and through the Gooch crucible, a vacuum such



as that obtained with the Bunsen filter pump is employed. While there is no risk with the use of the Gooch crucible, with the use of the filter paper there is risk of bursting it when the pump is used. It is necessary to support the filter-paper on a tough cone of filter-paper and then apply suction. Platinum cone also can be used to support the paper on.

As a further aid to rapid filtration, there are Jena glass sintered filters. Unlike the Gooch crucibles, they do not take time to get ready. The filtering medium is powdered glass, carefully sifted and heated to its sintering point without admixture with any bonding material. It is serviceable for ignition at temperatures of about  $600^{\circ}$  C. It is used very much in the same manner as the Gooch crucible, applying suction with the Bunsen filter-Pump.

A new Jena glass sintered crucible is cleaned with water, dried in an air oven at  $110^{\circ}$  C. and then heated gradually to  $600^{\circ}$  C. in an electric furnace. It is withdrawn from the furnace, cooled in a desiccator and weighed. It is then used for filtering off the ppte., washed with the appropriate wash liquids, dried at  $110^{\circ}$  C., slowly raised to  $600^{\circ}$  C. in an electric furnace, cooled in a desiccator and weighed. The difference between this weighing and the original, gives the weight of the precipitate from which the percentage of the constituent sought is calculated. In case the crucible is required for filtering off a precipitate of identical composition a second time, no time need be lost in washing the ppte. off the crucible, drying it, etc. . It may be put into use straight away. In case a ppte. having a composition different from the one already deposited, is to be filtered off, clean the crucible by dissolving the ppte. in a suitable solvent, wash with water, dry, heat to  $600^{\circ}$  C., cool and weigh. Then filter off the ppte. and dry.

These Jena glass sintered filters are made having different grades of porosity. The following are the particulars regarding purposes for which they are used:—

Grade of Porosity No.	Size of Pores in microns. (1 micron = $\frac{1}{1000}$ mm.)	Purpose.
1	100—120	Filtration of very coarse precipitates such as $\text{SiO}_2$ , $\text{Fe}(\text{OH})_3$ , $\text{Al}(\text{OH})_3$ , etc.
4	5—10	Filtration of very fine, precipitates such as $\text{BaSO}_4$ , $\text{CaC}_2\text{O}_4$ , $\text{CuCNS}$ , $\text{Cu}_2\text{O}$ , etc.

### Laboratory Reagents.

The reagents for analysis are sold in different grades of purity. The following table shows the names adopted by three reputed Chemical Supply Houses for indicating the quality of their products:—

Name adopted by the British Drug House, England.	Name adopted by the firm of E. Merck, Germany.	Name adopted by Baker Adamson, U. S. A.	Name adopted by the Fine Chemicals Section, Dept. of Industrial Chemistry, B. H. U.
1. Analytical Reagent, abbreviated to A. R.	Guaranteed Reagent, abbreviated to G. R.	Analysed.	Extra Pure.
2. Pure	Pure	—	—
3. Technical	Commercial	—	Commercial.

Any of the brands indicated in the horizontal row (1) may be used for quantitative analysis. For the

preparation of gases like  $\text{H}_2\text{S}$ ,  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , etc., those shown in ( 2 ) may be acted on by appropriate reagents of quality shown in ( 3 ).

The distilled water used in analytical work should occasionally be tested for its freedom from impurities such as chlorides, sulphates, etc. and also for total matter in solution. The last is determined by evaporating one litre of the water in small quantities at a time in a platinum dish. If any is found, the water is to be rejected.

Throughout this book where water is mentioned as a reagent, only distilled water is to be used.

Solid Reagents for analysis are received from the Chemical Supply Houses in corked or in glass stoppered bottles. The corks and the stoppers are coated with paraffin wax to prevent contamination by the packing material in the box in which they are shipped, and to ensure air tightness. To open the corked bottles, no cork-screw should be used, as the use of this makes a hole in the cork, exposing the chemical to air and dust. The wax is scraped off with a pen-knife, preferably stainless, and the pointed end passed round all along the edge of the cork close to the neck of the container with a lifting motion. By this means, the same cork can be used to close the mouth of the container, all that is necessary being to apply a coating of molten wax with a brush, after transfer of the required quantity, for day to day use, to a small size bottle in the Laboratory.

Liquid reagents like the concentrated mineral acids, inflammable liquids like carbon di sulphide, benzene, ethyl ether, etc. are received in containers like Winchester quart bottles or narrow mouthed bottles closed by means of stoppers, brushed over with molten wax. If

on giving a few strokes with a wooden rod, they do not open, i. e. the stoppers do not turn, pass round the neck of the bottle several turns of a strip of cloth about 1" broad and hold it in position by putting a knot on. Pour hot water on to the cloth bandage repeatedly until the wax melts and the stopper turns in its seat. Remove the stopper, wipe off the wax with a clean duster and place it in position when the neck is cold. On no account should a naked flame be applied to the neck nor should hot water be poured on the stopper. Stopcocks of burettes, gas analysis apparatus, etc. are opened in the same manner. Pouring a few drops of ether succeeds sometimes by dissolving off the vaseline on them.

Ammonia solutions are received in containers closed by means of rubber stoppers which are held in place by wire. In cold countries, there may not be any great risk in opening them. But in hot countries the gas which has been disengaged from the solution is held under pressure and on opening the stopper, one gets gassed. To avoid this, the bottle should be placed in a bucket of water cooled to about 5° C. by ice, or, in the absence of ice, by adding ammonium chloride or potassium nitrate to the water in the bucket, sufficient in quantity to bring the temp. to 5° C., for at least an hour to allow time for the contents to reach 5° C. and then opened.

In the absence of measuring cylinders for measuring out volumes of reagents for dissolving ores, metals, alloys, etc. substitutes can be improvised as follows:—

Apply with a brush a coating of molten paraffin wax about 1 cm. wide all along the entire length of a clean, dry test tube. Add to the test tube 5 ml. of water from a burette. Make a scratch with the pointed

end of a pin at the level at which the water stands in the test tube. Repeat adding water and making the scratch marks at intervals of 10, 15, 20, 25, etc., ml. The numbers 5, 10, 15, etc. are also marked on the wax with the pin. In a small platinum crucible (or in a porcelain crucible lined inside and out with wax by immersing it in molten wax and pouring out the surplus wax,) take 5 ml. of hydrofluoric acid, add 6 ml. of water, dip a tuft of cotton wool held at the end of a broom stick, 6" long, into the HF and apply the acid to the marks made. Keep the test tube in a warm place for 10-15 minutes, allowing time for the acid to act on the glass. Immerse the test tube in a boiling water bath until the wax melts off its surface. If properly done, the marks will be seen very clearly on taking out the test tube from the bath.

Take care that the acid does not come into contact with the fingers. There is much pain and one cannot use them for about a week if the acid comes into contact with them.

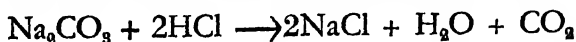
## CHAPTER II

Determinations involving Acidimetry and Alkalimetry.

### EXPERIMENT 1.

Determination of the number of grams of hydrogen chloride contained in 100 gms. of the concentrated acid provided on the Working-Bench and preparation of acid of 1.12 S. G. from acid of 1.2 S. G.

**Principle:**—This determination is based on the neutralization of the acid, suitably diluted, with a standard solution of sodium carbonate (in distilled water) using methyl orange as indicator. The reaction taking place is represented by the following equation:—



Clean a weighing bottle first with tap-water and then rinse with distilled water. Allow the water to drain, pass a current of hot air into the bottle to dry it, and cool in a desiccator.

*Step 1.* Introduce two hornspatulafuls of chemically pure anhydrous sodium carbonate into the bottle. Weigh exactly.

Shake off some of the carbonate into a clean beaker of 200 ml. capacity, about 1.5—1.6 gms. and weigh the tube again. If considerably less than 1.5 gms. has been transferred, transfer more and weigh. A few trials will enable one to get at the correct quantity. Reweigh the tube exactly. Difference between the two weighings yields the amount of carbonate transferred to the beaker.

*Step 2.* Dissolve the carbonate in 50 ml. distilled water and transfer to a clean 250 ml. measuring flask. Rinse the beaker 4 or 5 times, each time using about

10 ml. of water, and transfer the rinsings to the measuring flask. Make up to the mark exactly. Mix the contents to the flask well by shaking. To do this, close the mouth of the flask by means of a tightly fitting cork, invert it and bring it to the erect position. Repeat this five or six times. Alternatively, pour the content of the flask into a clean and dry beaker and transfer to the flask. Repeat pouring back and forth 3 or 4 times. Rinse a clean 20 ml. pipette with the solution by sucking it up to the mark and then throwing it away. Suck once again. Bring exactly to the mark and transfer to a clean 200 ml. beaker. To remove the liquid adhering to the tip of the pipette, touch the side of the beaker with the tip and draw it up along the side. In this way the last portion will come out.

*Step 3.* Run 3.5 to 5 ml. of the concentrated HCl on the Working- Bench from a burette into a clean 500 ml. measuring flask. Note the exact volume of acid used. Dilute this volume of acid with distilled water and make up to the mark. Mix well by shaking 5 or 6 times.

*Step 4.* Clean a burette with tap-water. If it is not greasy, no drops of water will adhere to it when it is drained. If drops adhere, here and there, it is greasy. To remove the greasiness, run into the burette a warm mixture (40 to 50°C.) of potassium dichromate (10 to 15 gms.) and concentrated sulphuric acid (100 ml.) and let stand some minutes. Drain and wash a number of times with tap-water. Fill with the diluted hydrochloric acid made above (*Step 3*) and empty. Refill with the diluted acid. The burette thus filled is ready for use.

*Step 5.* Add from a dropping bottle 5 or 6 drops of methyl orange to the sodium carbonate solution in the beaker. The solution becomes yellow. Run the acid with constant stirring, first somewhat rapidly, and then slowly until the solution becomes slightly red. If the titration is carried with a sheet of white paper underneath the beaker, the change of colour from yellow to light red is indicated more sharply. A porcelain basin is best for carrying out the titration.

**Record of results and method of calculation:**

weight of weighing bottle with  $\text{Na}_2\text{CO}_3$  = 18.7615 gms.  
 " " " " " after emptying = 17.4365 gms.  
 Weight of  $\text{Na}_2\text{CO}_3$  = 1.3250 gms.

1.3250 gms. dissolved in water and made up to 250 ml. . Strength of the solution is 0.1N. 3.5 ml. of conc. HCl were diluted to 500 ml.

*Titration :*

0.1 N  $\text{Na}_2\text{CO}_3$

(1) 20 ml.

(2) 20 ml.

HCl	
Final Reading . . . . .	25.0
Initial Reading . . . . .	0.0
	<hr/> 25.0
Final Reading	25.0
Initial Reading	0.0
	<hr/> 25.0

The strength of the diluted HCl is  $\frac{20}{25} 0.1\text{N} = 0.8 \times 0.1\text{N}$

The strength of the concentrated acid is  $\therefore \frac{0.8 \times 500}{3.5} 0.1\text{N}$

or 11.43 N.

The specific gravity of the same conc. HCl as measured by a hydrometer is 1.18.

100 ml. of the acid weigh 118 gms.



1000 ml. or 1180 gms. of the conc. acid contain  $11.43 \times 36.5$  gms. HCl.

100 gms. of the acid contain  $\frac{11.43 \times 36.5 \times 100}{1180}$  or  
35.35 gms. HCl.

The table of strengths of the common mineral acids against their specific gravities is constructed after conducting experiments as detailed above, starting with acids of different densities. With the help of such a table it is easy to prepare an acid of any required strength or specific gravity, starting from an acid of higher strength and with known specific gravity.

An example will make the method of calculation clear.

Given conc. HCl of 1.2 S. G., suppose it is required to prepare one litre of acid of 1.12 S. G.

From the Table of the S. G. of acids, we find that 1.20 S. G. acid contains 39.11 gms. per 100 gms. and that 1.12 S. G. acid contains 23.80 gms. per 100 gms.

39.11 gms. HCl are present in 100 gms. or  $\frac{100}{1.2}$  ml.

of the conc. acid. 1000 ml. of the acid to be prepared will weigh  $1000 \times 1.12$  or 1120 gms. and will contain  $\frac{23.8 \times 1120}{100}$  gms. HCl.

39.11 gms. HCl are present in 100 gms. conc. HCl.

i. e. in  $\frac{1}{1.2} \times 100$  ml. conc. HCl.

$\frac{23.8 \times 1120}{100}$  gms. HCl will be present in

$\frac{100 \times 23.8 \times 1120}{39.11 \times 1.2 \times 100}$  i. e. 567.9 ml. conc. HCl.

Volume of water to be added to 567.9 ml. conc. HCl to bring it up to 1000 ml. =  $1000 - 567.9$  i.e. 432.1 ml.

*Notes :—*The beaker into which the sodium carbonate is weighed, the measuring flasks, the pipette and the burette used in this and the following experiments should, after washing with tap-water, be rinsed 2 or 3 times with small quantities of distilled water. 5 ml. of it for each rinsing are enough. The rinsing is particularly necessary in this experiment, as the tap-water is alkaline due to the presence of carbonates.

Measuring cylinders and other vessels used for measuring out strong acids should be filled with tap water and emptied at least six times before they are used for measuring out other liquids.

2. When pure anhydrous sodium carbonate is not available, it is prepared from pure sodium bicarbonate as follows :—Half fill a clean platinum crucible with the substance. Introduce a thermometer into the crucible so that the bulb is completely surrounded by the chemical. Embed the crucible in a sand-bath heated by means of a Bunsen burner so that the sand comes on the outside of the crucible to the level to which it has been filled with the bicarbonate. When the temperature is kept between  $270^{\circ}$ - $300^{\circ}$ C. for half an hour, the bicarbonate changes completely to carbonate. Cool the crucible and contents in a desiccator and then use. The beaker into which the sodium carbonate is weighed need not be dried.

3. It is necessary to dilute the concentrated HCl so that the diluted acid has approximately the same strength as the carbonate solution. It is only when the volumes of the two solutions used for titration are nearly equal and about 20 ml. that the percentage

errors in taking the readings of the burette are small and negligible. This is a point that should be borne in mind in all subsequent work.

4. Owing to the passing of hydrogen chloride into the atmosphere, (the fuming observed, when the stopper from a bottle of the conc. acid is removed, is due to the escape and the subsequent solution of the gas in the water-vapour present in the atmosphere) the method described above, while not very accurate, is sufficiently so for all practical purposes.

5. Methyl orange:—Dissolve 0.02 gm. in 100 ml. hot water. Let stand and filter off any residue. Use the clear filtrate.

6. As the acid of standard strength obtained in this Expt. will be required in the experiments to follow, stock the same in a 250 ml. glass-stoppered bottle. Rinse the bottle twice with the acid before transferring. Paste a label showing the strength and the date of preparation.

7. In the preparation of the dilute acid of S. G. 1.10 from the concentrated acid, the assumption is made that there is no volume change accompanying dilution.

8. To remove greasiness from glass measuring vessels, they are filled with a warm mixture of concentrated  $\text{H}_2\text{SO}_4$  (100 ml.) and (10-15) gm. powdered potassium dichromate, allowed to stand 5-10 minutes, emptied and then washed with tap-water. As the mixture of dichromate and sulphuric acid can be used over and over again, it should not be emptied into the sink but should be preserved or returned to the Stock bottle kept for common use in the Laboratory.

## EXPERIMENT 2.

Determination of the percentage of NaOH and  $\text{Na}_2\text{CO}_3$  in commercial caustic soda sticks.

**Principle:—**

A known weight of the sticks is dissolved in water and the solution made up to a known volume. In one aliquot part of the solution, the total alkali present is obtained by titration with a standard acid; from another part, the carbonate present is precipitated as  $\text{BaCO}_3$  by the addition of  $\text{BaCl}_2$ , the precipitate filtered off and the alkali present in the filtrate determined by titration with the same standard acid as before. From the difference between the volumes of the acid used, the amount of  $\text{Na}_2\text{CO}_3$  is calculated. The volume of acid used for the second titration yields the amount of NaOH.

Solutions required:—(1) 20%  $\text{BaCl}_2$  solution

(2) Methyl orange. See para 5 of 'Notes', under Expt. 1.

**Procedure :**

*Step 1.* Remove one stick of the commercial caustic soda from the reagent bottle by means of a pair of brass tongs. Break it up in a dry porcelain mortar with a pestle into small pieces, introduce the broken pieces into a clean, dry weighing bottle. Weigh the bottle with contents exactly. Transfer about 4 gms. into a 150 ml. beaker. Weigh the bottle again. If the weight of soda transferred is considerably less than 4 gms., transfer more until it is about 4 gms. Weigh to a fifth of a mgm. Dissolve in 40-50 ml. water and transfer the solution to a measuring flask of 250 ml. capacity. Rinse the beaker 5 or 6 times with distilled water, each time using about 10 ml. Transfer the rin-

sings to the measuring flask. Add water to the mark in the flask. Mix thoroughly the contents of the same by shaking. Draw off by means of a 50 ml. pipette 50 ml. of the solution and empty it into a No. 6 (250 ml.) beaker. Add 5-6 drops of methyl orange. Fill a burette with the standard HCl prepared in Experiment 1. If none of that acid is left, acid 0.2N or 0.1N strong should be prepared in the manner shown thereunder. Titrate the solution in the beaker by running the acid, first somewhat rapidly, and then, somewhat slowly, until the yellow colour changes to pink. Repeat the titration 3 times. The three volumes should agree to within 0.1-0.2 of one ml.

*Step 2.* Transfer to a second No. 6 beaker 50 ml. of the solution of caustic soda. Add to it, by means of a 5 ml. pipette,  $\text{BaCl}_2$  solution, in small quantities at a time. Allow the precipitate formed to settle before making a second addition of  $\text{BaCl}_2$  solution. Continue adding  $\text{BaCl}_2$  to the clear supernatant liquid as long as a precipitate forms at the point of contact of the two liquids. In order that the precipitate which has settled may not be disturbed, it is necessary to allow  $\text{BaCl}_2$  solution to run along the side of the beaker. When no more precipitate forms, filter off the same, receiving the filtrate in a No. 6 beaker. Wash the precipitate and beaker 5 or 6 times with water. Titrate the filtrate and washings with the same standard HCl as was used in the first part of the experiment. Use methyl orange as indicator.

### Record of Results and Calculation.

Weight of sticks+weighing bottle	= 15.8456	gms.
shaking off a little into the beaker	} = 12.7496	gms.
Weight of sticks used		

This was dissolved and the solution was made up to 250 ml.

**Titration:**

<u>NaOH + Na<sub>2</sub>CO<sub>3</sub></u>	<u>HCl ( 0.164 N )</u>
( 1 ) 50 ml.	87.5 ml.
( 2 ) 50 ml.	87.6 ml.
( 3 ) 50 ml.	87.5 ml.
Average volume HCl used	=87.5 ml.

Titration of a fresh 50 ml. portion after treatment with BaCl<sub>2</sub> solution and filtration showed a consumption of 83.9 ml. of 0.164N HCl.

Vol. of 0.164 N-HCl required for reacting with the NaOH present in the sticks is 83.9 ml.

$$\text{Hence, \% NaOH} = \frac{83.9 \times 250}{50} \times \frac{40 \times .164}{1000} \times \frac{100}{4.05} = 67.95$$

Vol. of 0.164 N HCl required for reacting with the Na<sub>2</sub>CO<sub>3</sub> present in the solution will be 87.5—83.9 or 3.6 ml.

3.6 ml. of 0.164 N-HCl is chemically equivalent to 3.6 ml. of 0.164 N-Na<sub>2</sub>CO<sub>3</sub>

$$\text{Hence \% Na}_2\text{CO}_3 = \frac{3.6 \times 250 \times 0.164 \times 100 \times 106}{50 \times 1000 \times 4.05 \times 2} = 3.86$$

**NOTES:—**

The addition of a large excess of BaCl<sub>2</sub> will lead to the following reaction:— $2\text{NaOH} + \text{BaCl}_2 \rightarrow \text{Ba}(\text{OH})_2 + 2\text{NaCl}$ . Ba(OH)<sub>2</sub> thus formed would be titrated by the acid, provided the titration is proceeded with, without delay. In the method as described above no time should therefore be lost in filtering off BaCO<sub>3</sub> and titrating the filtrate, as otherwise Ba(OH)<sub>2</sub> will form BaCO<sub>3</sub> by taking CO<sub>2</sub> from the Laboratory atmosphere and the value for NaOH will be lower than what it really is.

The titration may be carried out without filtering off the precipitate provided the addition of acid is made slowly. The first substance to be neutralized is the sodium hydroxide, the acid attacks the precipitate when all the hydroxide is used up. But this point is indicated by the indicator. In the hands of a beginner, the method described under 'Procedure' leads, however, to more reliable results.

### EXPERIMENT 3.

Determination of the percentages of NaOH and  $\text{Na}_2\text{CO}_3$  in caustic soda sticks:—( The double indicator method )

#### Principle:—

When a solution containing NaOH and  $\text{Na}_2\text{CO}_3$  is titrated with standard hydrochloric acid using phenolphthalein as the indicator, the whole of the caustic alkali and one half of the carbonated alkali is neutralized, when the pink colour of the solution disappears. If, at this stage, methyl orange is added as indicator and the titration with acid continued until the colour changes to light red, the remaining half of the carbonated alkali is neutralized. In other words, the pink colour due to phenolphthalein is destroyed when NaCl and  $\text{NaHCO}_3$  are formed. The latter reacts with methyl orange yielding a yellow colour and the acid is added until the change to light red appears.

Indicators:—( 1 ) Phenolphthalein: Dissolve 0.1 gm. of the solid in 100 ml. of 95% ethyl alcohol i. e. 95 ml. of the pure alcohol and 5 ml. of water.

( 2 ) Methyl orange. The same as in para 5 of Notes, Experiment 1.

**Procedure:—**

Same as in Experiment 2 until 50 ml. of the caustic soda solution are transferred to a No. 6 beaker. Add 3-4 drops of phenolphthalein and continue adding standard HCl until the liquid becomes colourless. Add 3-4 drops of methyl orange to the contents of the beaker and finish the titration as usual, i. e. until a light red colour appears.

*Record of Results and Calculation:* Weight of sticks=4.05 gms. The solution was made to 250 ml.

NaOH+Na <sub>2</sub> CO <sub>3</sub>		0.164 N-HCl	0.164 N-HCl
(1) 50 ml.	87.7 ml.	(After adding methyl orange)	1.8 ml.
(2) 50 ml.	87.8 ml.	„	1.7 ml.

To avoid errors in reading the burette when the volume used is small as in the last part of the above expt. the acid was reduced to 1/10 of its strength for titration after introducing methyl orange. This is done by pipetting off 10 ml. of 0.164 N-HCl into a 100 ml. measuring flask, diluting with water to the marking and mix thoroughly before use.

NaOH+Na <sub>2</sub> CO <sub>3</sub>	0.164 N-HCl	0.0164 N-HCl
50 ml.	87.7 ml.	17.6 ml. (after introducing methyl orange.)

Volume of Na<sub>2</sub>CO<sub>3</sub> in 50 ml. solution =  $2 \times 17.6$  ml. of 0.0164 N-Na<sub>2</sub>CO<sub>3</sub>.

% of Na<sub>2</sub>CO<sub>3</sub> in the sample supplied

$$= \frac{3.52 \times 53 \times 164 \times 250 \times 100}{1000 \times 50 \times 4.05} = 3.78$$

$$\% \text{ NaOH} = \frac{83.94 \times 250 \times 40 \times 100}{50 \times 1000 \times 4.05} = 67.98.$$

NOTE:—Sodium bicarbonate yields a colourless solution with phenolphthalein, only when the temperature is at 0°C. At room temperature a pink colour appears. The titration by the method described in this experiment will yield accurate results only when the temperature



of the solution titrated is kept at  $0^{\circ}\text{C}$ . by surrounding the titrating beaker with ice. As it is difficult to secure ice at all times of the year in this country, the method described in Experiment 2 is to be preferred.

#### EXPERIMENT 4.

Determination of Temporary and Permanent Hardness in water.

*Introductory Notes:*—The presence of calcium and magnesium bicarbonates and sulphates in solution in a sample of water leads, when such water is fed into boilers, to the formation of a crust on the plates, thus preventing an efficient transfer of heat to the water. In large industrial establishments, the damage done to boilers is considerable and the waste of fuel high, when such waters are fed into them direct, without previous treatment. From the point of view of drinking purposes, the presence of  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$  to the extent of 10-15 grains per gallon is beneficial to the health of man but the presence of  $\text{CaSO}_4$ , even to the extent of 3-4 grains per gallon, is not desirable, as vegetables and pulses are not properly cooked in water containing them.

Determination of Temporary Hardness: This is due to the presence of  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$ .

**Principle:**—

When a standard solution of  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  is run into a measured volume of the sample of water under examination, the bicarbonates are neutralized by the acid and an excess of the acid will colour the solution red, when methyl orange is added as indicator.

**Procedure:**—

Take 100 ml. of the water in a 250 ml. porcelain dish or casserole. Add 3 to 4 drops of methyl orange,

run in  $N/50 \text{ H}_2\text{SO}_4$  from a burette, drop by drop, stirring with a glass rod all the while, until the solution turns red.

$$1 \text{ litre } N/50 \text{ H}_2\text{SO}_4 = 1 \text{ litre } N/50 \text{ CaCO}_3 \\ = 1 \text{ gm. CaCO}_3$$

$$1 \text{ ml. } N/50 \text{ H}_2\text{SO}_4 = 0.001 \text{ gm. CaCO}_3$$

Temporary Hardness is generally reported in grains of  $\text{CaCO}_3$  per gallon.

One gallon of water at  $60^\circ\text{F}$ . weighs 70,000 grains.

100 ml. of water weigh 100 gms.

If in the experiment 100 ml. required 30 ml. of  $N/50 \text{ H}_2\text{SO}_4$ , then the number of grams of  $\text{CaCO}_3$  in 100 gms. of the sample  $= 0.03 \text{ gm}$ .

If instead of 100 gms. we had taken 100 grains of water, the amount of  $\text{CaCO}_3$  in it would be 0.03 grain.

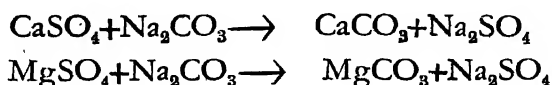
For convenience in measuring, we take 100 ml. of the sample : weighing 100 grains of water will take time ; besides it is too small a weight to experiment with, being about 6 ml. Hence 100 ml. of the sample of water are used for the determination. But the results are reported in terms of grains per gallon.

Thus, the temporary hardness of the water under examination is  $0.03 \times \frac{70,000}{100}$ , i.e., 21 grains per gallon. This system of expressing the results is adopted in England.

*Determination of Permanent Hardness:* Permanent hardness is caused by the presence of sulphates and chlorides of calcium and magnesium.

The results are however expressed in terms of grains of calcium carbonate per gallon, one formula weight of  $\text{CaSO}_4$  being chemically equivalent to one formula weight of  $\text{CaCO}_3$ .

**Principle:—**When a sample of water under test is treated with an excess of a standard solution of  $\text{Na}_2\text{CO}_3$  and the mixed solution evaporated to dryness, the following reactions take place :—



The residue is dissolved in distilled water and the solution is filtered off and the filtrate titrated with standard acid using methyl orange as indicator. The amount of standard  $\text{Na}_2\text{CO}_3$  used for the above reactions is a measure of the permanent hardness of the sample of water.

**Procedure:—**Measure 100 ml. of the sample of water with a 100 ml. measuring cylinder into a Jena glass beaker or a casserole. Add 25 ml. of  $N/10 \text{Na}_2\text{CO}_3$ . Evaporate to dryness. Cool. Redissolve in about 5-10 ml. water. Filter, wash twice. Use 5 ml. water each time. Titrate the cold filtrate with  $N/10 \text{H}_2\text{SO}_4$  using methyl orange as indicator.

Results : 25 ml.  $N/10 \text{Na}_2\text{CO}_3$  were added.

22.5. ml.  $N/10 \text{H}_2\text{SO}_4$  were required for 'back titration'.

2.5 ml.  $N/10 \text{Na}_2\text{CO}_3$  has been used up to react with  $\text{CaSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{CaCl}_2$  and  $\text{MgCl}_2$ .

Hence 2.5 ml.  $N/10 \text{Na}_2\text{CO}_3 = 2.5 \text{ ml. } N/10 \text{CaCO}_3$   
 $= 2.5 \times .005 \text{ gm. CaCO}_3$   
 $= 0.0125 \text{ gm.}$

100 ml. of water contain 0.0125 gm.

100,000 „ „ „ 12.5 gms.  
 Permanent hardness in the }  $= 12.5 \times .7 \text{ grains per}$   
 sample of water }  $= 8.75$  „ „ „

NOTES :—(1) There is no direct titration method of determining the permanent hardness in a sample of water. The method adopted here is one which is frequently employed in analytical operations. Introduction of a measured excess of a standard reagent and the titration of the amount of the same not used in a reaction are the features of the method. One is said to '*back-titrate*' the unused amount and the process of so doing is '*back-titration*'.

(2) Owing to the solubility of  $\text{MgCO}_3$  formed as a product of the reaction, it is necessary to evaporate to dryness after the addition of  $\text{Na}_2\text{CO}_3$ . This operation takes time. The use of a mixture of standard  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$  solutions for the purpose has the advantage that evaporation to dryness is not necessary as the very insoluble  $\text{MgO}$  is formed thereby instead of the somewhat soluble  $\text{MgCO}_3$ .

(3) The use of freshly boiled and cooled distilled water is recommended for extracting the dry residues, as any dissolved  $\text{CO}_2$  in distilled water that has been stored for some time, will tend to dissolve the precipitated  $\text{CaCO}_3$  and  $\text{MgCO}_3$  and thus lead to inaccurate results.

(4) In the case of certain waters, the volume of acid used for '*back titration*' is greater than the volume of  $N/10 \text{ Na}_2\text{CO}_3$  originally introduced. This is because of the fact that those waters contain sodium carbonate in solution. The water from the wells on the University grounds furnishes a good example of such waters. The amount of sodium carbonate per gallon is obtained by calculating as follows :—Subtract the number of ml. of  $N/10 \text{ Na}_2\text{CO}_3$  introduced from the number of ml. of  $N/10 \text{ H}_2\text{SO}_4$  used for back titration.

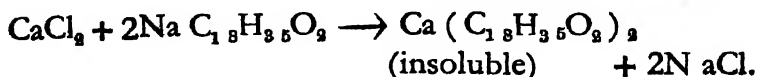
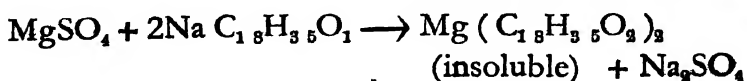
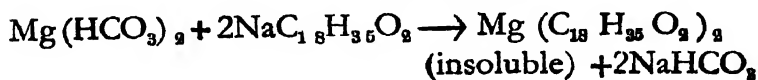
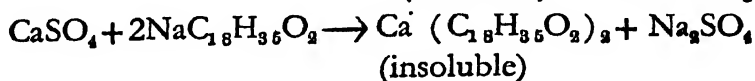
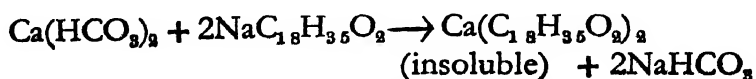
$$1 \text{ ml. } N/10 \text{ H}_2\text{SO}_4 = 0.0053 \text{ gm. } \text{Na}_2\text{CO}_3$$

(5) An alternative method for the determination of the hardness of a sample of water is what is known as the 'Soap Method'. It is described in Experiment 5.

### EXPERIMENT 5.

Determination of the temporary and the permanent hardness of a sample of water by the 'Soap Solution' method :—

**Principles :—**(1) When an alcoholic solution of soap, which may be considered as sodium stearate, is added to water holding the bicarbonates, sulphates and chlorides of calcium and magnesium in solution, the following reactions take place :—



The soap solution begins to yield a lather with the water only after the salts in solution have reacted in the above manner. Hence, the volume of soap solution used to produce a permanent lather is a measure of the hardness of the water. (2) Also, the temporary hardness causing salts, namely, the bicarbonates of calcium and magnesium, are decomposed by boiling. They separate as  $\text{CaCO}_3$  and  $\text{MgCO}_3$ .



*Solutions required*:—(1) Standard Hard Water. Prepare 1 litre of standard hard water as follows:—Dissolve 0.2 gm. of chemically pure calcium carbonate in 10 ml. of 1.1 S. G. HCl diluted with 20 ml. water in a No.2 porcelain basin or casserole and evaporate to dryness on a water bath. Redissolve the residue, when cold, in 25 ml. water. Transfer solution to a 1 litre measuring flask. Rinse and transfer the rinsings to the flask and make up to the mark. Mix well by shaking. When a large volume of standard solution is to be made thoroughly homogeneous, an efficient and quick method is to dry a large size beaker and pour into it the solution from the measuring flask. Again the solution is poured back into the flask and in this way by pouring forth from the flask and back into it 3 or 4 times, a thorough mixing is effected. The hardness of the standard water so prepared is 14 grains of calcium carbonate per gallon.

2. *Clark's Soap Solution*:—Grind 150 parts of lead plaster (lead oleate) in a porcelain mortar with 40 parts of anhydrous potassium carbonate. When well mixed, add a little *neutralized* methylated spirit and again grind until a smooth cream is obtained. Add 150-200 ml. more of the neutralized methylated spirit, stir, allow to stand for about 10 minutes and filter. Dilute the stock solution thus obtained as follows:—Mix 2 parts by volume of neutralized methylated spirit with 1 part by volume of distilled water. Add to the stock soap solution sufficient of the mixture of spirit and water so that 14.25 ml. of the diluted soap solution are required to give a permanent lather with 50 ml. of the standard hard water. The following example will make clear how the dilution is done:—Suppose 50 ml. of Solution (1) required 1 ml. stock soap solution to give a per-

manent lather. Add 13.25 ml. of the diluted spirit—water mixture to each ml. of the stock soap solution.

**Procedure:**—Pipette off 50 ml. of the sample of water into a 250 ml. glass-stoppered bottle. Run from a burette the diluted soap solution, 1 ml. at a time, and shake after each addition. Lay the bottle on its side on the Working-Bench. If the lather disappears quickly, add more of the solution and shake. Repeat adding soap solution until a lather persisting for about 3 minutes is obtained when the bottle is laid on its side on the table. By reference to Table No 6, find out the hardness of the sample of water. The hardness obtained is the 'Total Hardness'. To ascertain the temporary and the permanent hardness separately, proceed as follows:—

Boil 50 ml. of the sample of water in a No. 4 beaker for half an hour. Add from time to time distilled water to make up for the water lost by evaporation. Filter off the residue. Collect the filtrate in a 250 ml. glass stoppered bottle. Wash the beaker and residue 2 or 3 times with freshly boiled and cooled distilled water. To the cooled filtrate add from a burette soap solution, in small quantities at a time, shake and proceed until a permanent lather lasting for 3 minutes is produced. From the table, read the hardness corresponding to the volume of soap solution used. The figure obtained represents the permanent hardness. To obtain the temporary hardness, subtract the 'Permanent Hardness' number from the 'Total Hardness' number.

### **Record of Results and Calculation:**

Volume of sample taken 50 ml.

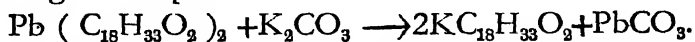
Soap solution added to yield Total Hardness = 10.0 ml.

Total Hardness = 9.32 degrees Clark.

Soap solution added to yield Permanent Hardness = 4.0 ml.  
Permanent hardness = 3.2 degrees Clark.

Temporary Hardness = 9.32 — 3.2 = 6.12 degrees Clark.

NOTES:—( 1 ) The employment of a perfectly neutral soap is necessary for preparing the soap solution. As the commercial soaps are almost always alkaline, a neutral potassium soap solution is prepared in the manner described. Potassium oleate which is thereby formed behaves in exactly the same way as sodium stearate figured in the reactions shown under the heading 'Principle'.



A perfectly neutral soap under the name of 'Sofnol Soap Powder' has been placed on the market by Messrs. Gallenkamp & Co., London.

( 2 ) The spirit used must be neutralized with 0.1N—NaOH, phenolphthalein acting as indicator. The acids present in the spirit are organic acids. These, if not neutralized, will react with the carbonates in the water and thus give low values for "Temporary Hardness".

( 3 ) Dilution of the stock soap solution in the manner described with spirit-water mixture is necessary inasmuch as the precipitate of calcium and magnesium stearate or oleate formed is insoluble in such a mixture.

( 4 ) This method does not yield accurate results when the sample of water under test contains both  $\text{Mg} ( \text{HCO}_3 )_2$  and  $\text{Na}_2\text{CO}_3$ . The two appear to form a double compound which is not decomposed by boiling, with the result that all the temporary hardness is not removed by boiling. Hence even in samples of water which do not contain any  $\text{CaSO}_4$  or  $\text{MgSO}_4$ , permanent hardness is indicated by this method but the one described in Experiment 4 does not suffer from this defect and hence it is being more widely used.



## EXPERIMENT 6.

Retesting of softened water.

Introductory:—

Water is softened by the addition of lime and  $\text{Na}_2\text{CO}_3$ . As considerable excess of these reagents will attack the gun-metal of which certain boiler fittings are made and as they also cause considerable foaming, only quantities of these, sufficient for the removal of the hardness present, should be added. A check on the excess of any softening chemical that may be present is, therefore, necessary.

**Principle:**—When a standard acid is added to the softened water in the presence of methyl orange as indicator, the excess of alkali or alkaline carbonate is neutralized. The volume of acid used is a measure of the excess of softening chemical. This excess is expressed in terms of grains of  $\text{Na}_2\text{CO}_3$  per gallon.

**Solutions and Reagents required:**—

(1) 1 litre water containing 20 grains per gallon of Temporary hardness. Water from one of the wells on the University grounds serves the purpose.

(2) 2 gms. quicklime (freshly ignited).

(3) 250 ml. of 0.02N—HCl.

**Procedure:**—Measure out 1000 ml. water with a measuring jar into a litre bottle having a glass stopper. Weigh into it 0.2–0.22 gm. of the freshly ignited  $\text{CaO}$ . Shake well for 10 minutes and let stand for half an hour and filter, or, filter off immediately about 500 ml. into a No. 8 beaker, cleaned and dried, using a dry filter paper and dry funnel. Rinse a 100 ml. pipette, or, a measuring jar, if a pipette is not available, with the filtrate. Pipette off 100 ml. into a No. 6 beaker, add

3-4 drops of methyl orange and drop from a burette 0.02N-HCl until the colour changes to a decided red. Repeat this twice. Take 100 ml. distilled water in a beaker, add 3-4 drop of methyl orange and run the acid until a red colour, of the same intensity as in the sample run, is obtained. Note the reading.

### Record of Results and Calculation.

1 litre water shaken with 0.2 gm. CaO and filtered.

*Filtrate*                      0.02N-HCl

(1)	100 ml.	5.0 ml.
(2)	100 ml.	5.1 ml.
(3)	100 ml.	5.1 ml.

100 ml. distilled water consume 0.3 ml. of 0.02N-HCl to give red colour of the same intensity.

Average volume of acid minus blank =  $5.1 - 0.3$  or 4.8 ml. 0.02N—HCl

$$4.8 \text{ ml. } 0.02N\text{-HCl} = 4.8 \text{ ml. } 0.02N\text{-Na}_2\text{CO}_3 \\ = \frac{53 \times 4.8}{50 \times 1000} \text{ gm. } ,,$$

$$100 \text{ ml. of softened water contains } \frac{53 \times 4.8}{50 \times 1000} \text{ gm. Na}_2\text{CO}_3$$

$$1 \text{ gallon of softened water contains } \frac{53 \times 4.8}{50 \times 1000} \times \frac{7}{10}$$

grains of  $\text{Na}_2\text{CO}_3$  i. e., 3.5 grains  $\text{Na}_2\text{CO}_3$ .

NOTES :—

(1) The alkalinity of the softened water is expressed generally in grains of  $\text{Na}_2\text{CO}_3$  per gallon. A number of trials on boiler waters have shown that only about 2-3 grains of alkalinity as  $\text{Na}_2\text{CO}_3$  per gallon are permissible in softened water.

(2) When very dilute solutions of acid and alkali are being titrated, the colour change from yellow to

red or vice versa is not very sharp. Hence in such cases a blank run is made using distilled water and the indicator, the volumes of these being nearly the same as in a sample run.

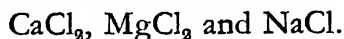
(3) The beaker in which the filtrate is collected need not be dried, provided the first runnings of the filtrate are used to rinse the same. By this means, weakening of the strength of the filtrate by the adhering of the water which was used to wash the beaker, is prevented.

(4) When the water contains permanent hardness, sodium carbonate should be substituted for CaO and the excess of sodium carbonate in the softened water determined exactly as above. When the water examined contains both temporary and permanent hardness, they are removed by adding lime and sodium carbonate and the softened water then examined as above.

## EXPERIMENT 7.

### Determination of the amount of Chlorine in water.

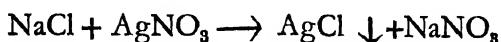
**Introductory** :—Chlorine is present in water in the form of one or more of the following compounds :—



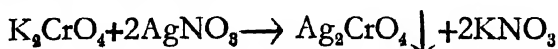
The presence of these in water which is to serve as boiler-feed is injurious to the life of the boiler. Under the conditions of temperature and pressure prevailing within it, a number of complicated chemical reactions take place resulting in the production of free HCl. This has a corrosive action on steel plates. The amount of chlorine as chloride in water meant for drinking purposes serves to indicate its contamination or otherwise by drainage.

**Principle** :—When the sample of water, rendered neutral by the addition of  $N/50 \text{ Na}_2\text{CO}_3$  or  $N/50$

$\text{HNO}_3$ , according as it is acid or alkaline, is treated with  $N/60 \text{ AgNO}_3$  run from a burette, the chlorine reacts as follows :—



The point at which this reaction is at an end is shown by the potassium chromate solution, introduced as an indicator at the commencement of the titration, turning red. The appearance of this colour is due to the formation of silver chromate as a precipitate. The reaction is as follows:—



#### **Solutions required:—**

1. Standard  $\text{AgNO}_3$ : Dissolve 0.5666 gms.  $\text{AgNO}_3$  in distilled water and make up to 200 ml. exactly. 1 ml. of this = 0.000591 gm. Cl.

2. Potassium chromate: Dissolve 1 gm. in 20 ml. water. Add  $\text{AgNO}_3$  Solution (1), from a burette until a slight precipitate appears. Let stand and filter. For each titration, use 1 ml. of the clear filtrate as indicator.

**Procedure:—**Measure out 100 ml. of the Laboratory tap-water into a porcelain basin by means of a graduated jar. As this water is alkaline, run  $N/50 \text{ HNO}_3$ , using methyl orange as indicator, until slightly pink. Note the volume of  $N/50 \text{ HNO}_3$  used. Reject the titrated liquid. Rinse the basin twice with distilled water. Into it measure out 100 ml. of the tap water as before. Without introducing methyl orange, run 1 ml. less than the volume of  $N/50 \text{ HNO}_3$  required to destroy the alkalinity. Introduce now 1 ml. of the chromate indicator and add the standard  $\text{AgNO}_3$  until a faint reddish coloration is seen.

**Example:—**

Suppose 100 ml tap-water required 40.0 ml.  $N/50$   $\text{HNO}_3$  for neutralization, methyl orange acting as indicator.

Take 100 ml. tap-water, add 39 ml.  $N/50$   $\text{HNO}_3$ , introduce 1 ml.  $\text{K}_2\text{CrO}_4$  indicator and run standard  $\text{AgNO}_3$  from a burette until red.

Volume used = 10.0 ml.

Grams Cl in 100,000 gms. water =  $1000 \times .000591 \times 10 \text{ gm.}$   
 $= 5.91 \text{ " gms.}$

Grains Cl per gallon =  $5.91 \times 0.7 = 4.137 = 4.1$

**NOTES:—**

(1) If the water is acid in reaction, the acidity must be destroyed by the addition of  $\text{Na}_2\text{CO}_3$ . As silver chromate is soluble in alkalies and acids, it is necessary to carry out the determination in a neutral, or only very slightly alkaline, medium such alkalinity being due to carbonate, not ammonia or sodium hydroxide.

(2) This determination is often helpful in enabling one to decide whether the concentration of the salts in solution in a boiler has reached a stage at which troubles due to overheating of tubes and priming occur. Thus if the feed water contains 4 grains of Cl per gallon and if the water from the boiler contains 400 grains of it per gallon, the water has been concentrated 100 times. If the amount of other sodium salts in the feed is known, the total solids in the water can be easily calculated. Thus in the feed water,

$\text{Na}_2\text{CO}_3 = 13.0$  grains per gallon.

$\text{NaCl} = 6.6$  " " " "

**Solids in feed water = 19.6**    „    „    „    .

Total solids in the water drawn from the boiler  
 $= 19.6 \times 100$  grains,  
 $= 1960$  grains.

The concentration is very high and will lead to troubles unless some quantity of water is run out and the volume run out made good by make-up water.

.(3) As it is difficult to get the end point sharply, the usual practice is to take 150 ml. distilled water in a basin, add 1 ml. chromate indicator and run the silver nitrate until a distinct red coloration is seen. 0.5-1.0 ml. may be required for the purpose. Run the silver nitrate solution into the sample of water until a red colour of the same intensity as in the blank is seen. Deduct the number of ml.  $\text{AgNO}_3$  used for the blank run and then calculate.

## CHAPTER III

### Determinations Involving Oxidation and Reduction Reactions.

#### EXPERIMENT 8.

#### Standardization of Potassium Permanganate Solution.

**Principle:**—In acid solutions containing reducing agents, the permanganate decomposes giving 5 gram-atoms of oxygen (equivalent to 10 gram-atoms of hydrogen) for every 2 gm. moles of the permanganate. Hence, a normal solution of  $\text{KMnO}_4$  will contain per litre of solution  $\frac{2\text{KMnO}_4}{10}$  or  $\frac{\text{KMnO}_4}{5}$  i.e. 31.6 gms.

With a view to facilitate calculations, a solution of  $\text{KMnO}_4$  of  $5/56 N$  strength is most often used in technical analysis.

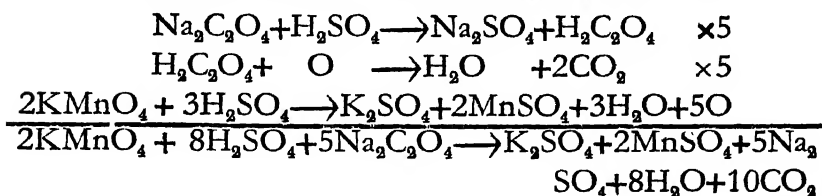
As it is somewhat difficult to obtain chemically pure permanganate and as the distilled water used almost always contains traces of organic matter which are oxidized by the permanganate, the most general practice of preparing a standard solution of it is as follows :—

Weigh out approximately 2.80 - 2.9 gms. of it in a clean, dry, weighing tube. Transfer to a beaker of about 1000 ml. capacity. Add distilled water almost to the brim. Mix thoroughly by pouring back and forth into a second beaker. Let stand for a day ( 24 hours ) and filter through asbestos into a brown bottle. Pour asbestos pulp on to a perforated porcelain plate or disc fitted to a funnel so as to form a layer 1-2 mm. thick.

The asbestos pulp is prepared as follows :—

Some long fibered soft asbestos is cut with a pair of scissors into  $\frac{1}{2}$  cm. length pieces and the cut pieces digested with 30–40 ml of conc. HCl in a basin in a boiling water-bath. The asbestos is then filtered off on a Buchner funnel and washed with distilled water until free from chloride. A small flock of the material is shaken vigorously with about 200 ml. water in a flask.

This solution is standardized against sodium oxalate solution. This substance is easily obtained in a state of purity, is not hygroscopic and does not contain water of crystallization. The reaction that takes place when permanganate solution is added to a hot solution of sodium oxalate acidified with dil.  $\text{H}_2\text{SO}_4$  is as follows :—



The strength of  $\text{KMnO}_4$  being about  $5/56$   $N$ , it is necessary that the strength of the oxalate solution must also be about  $5/56$   $N$ .

From the above reaction, it is clear that each gram-mole of  $\text{Na}_2\text{C}_2\text{O}_4$  requires 1 gram-atom of oxygen (=2 gram-atoms of hydrogen) for oxidation. Hence 1 litre of  $5/56$   $N$  strength of sodium oxalate will contain

$$\frac{\text{Na}_2\text{C}_2\text{O}_4}{.2} \times \frac{5}{56} = \frac{134}{2} \times \frac{5}{56} = 5.9821 \text{ gms.}$$

**Procedure :—**From 5.9–6.0 gms. of it are *exactly* weighed out into a 400 ml. beaker. 200 ml. of distilled water added and about 10 ml. of  $6N$  sulphuric acid is also added. The oxalate is brought into solution by heating to about  $70^\circ\text{C}$ ., then transferred to a measuring



flask of 1000 ml. capacity, the beaker rinsed with distilled water 3-4 times, the rinsings poured into the measuring flask, the contents of the flask cooled to the Lab. Temp. by cooling under the tap and the solution then made up to the mark with distilled water. The solution is then thoroughly mixed by pouring back and forth into a clean, dry beaker four or five times.

Pipette off 20 ml. of the oxalate solution into a 400 ml. beaker. Add 3-5 ml. of 6N-H<sub>2</sub>SO<sub>4</sub>, dilute to about 200 ml. with distilled water, heat to about 70°C. and run the permanganate solution from the burette, slowly at first, and then fairly rapidly, until the solution is coloured faintly pink. The mean of three titration values is taken in calculating the strength of the permanganate solution.

Enter the results thus :—

Weight of Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> = 6.000 gms. Dissolved in water and the solution made up to 1 litre exactly.

Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	KMnO <sub>4</sub>
20 ml.	0.8-21.1 = 20.3 ml.
20 ml.	1.2-21.5 = 20.3 "
20 ml.	2.0-22.3 = 20.3 "
Sum 60 ml.	60.9 ml.
Mean 20 ml.	20.3 ml.

**Calculation :—**The strength of the oxalate solution will be  $\frac{6.000}{5.9821} \times \frac{5}{56} N$ . The strength of the permanganate solution will, therefore, be  $\frac{20}{20.3} \times \frac{6.000}{5.9821} \times \frac{5}{56} N$ . 1 ml. of  $\frac{5}{56} N$ -KMnO<sub>4</sub> = 0.005 gm. Fe.

NOTES :—

(1) 1/4th or 1/5th of the quantities of KMnO<sub>4</sub> and Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> may be used instead of the weights mentioned

and the volumes of the solutions made should then be either 250 ml. or 200 ml. .

(2) As standard solutions of  $\text{KMnO}_4$  are required constantly in analytical work and as they fall in strength due to the action of sunlight, when they are stored in colourless bottles, amber-coloured or blackened bottles are recommended for storing the same. They should be glass-stoppered and protected from dust particles and from reducing gases such as  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ , etc.

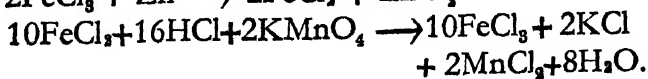
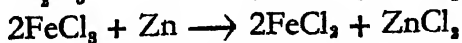
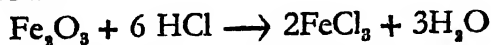
(3) A burette with a glass stop-cock is to be used with standard  $\text{KMnO}_4$  solution. The strength of the same falls when used in burettes with rubber tubing and pinch clamp due to the oxidation of rubber. As there is no such reaction between rubber and oxalate solution, it may be filled into a burette with rubber tubing and pinch clamp.

## EXPERIMENT 9.

### Determination of Iron in Iron Ore.

**Principle:**—The ore is brought into solution in  $\text{HCl}$  or in a mixture of  $\text{HCl}$  and  $\text{HNO}_3$ , in the case of a sulphide, and, in the latter case, the excess  $\text{HNO}_3$  driven off by evaporation with  $\text{H}_2\text{SO}_4$  to fuming. The ferric chloride or sulphate thus obtained is reduced by means of zinc to the ferrous condition. The ferrous iron solution is titrated with a standard solution of  $\text{KMnO}_4$  until a faint pink colour is obtained.

The reactions that take place on solution of hematite and on reduction and titration are represented as follows :—



### Introductory:—

The question that arises before starting an experiment like this is: What is the quantity of the ore that should be taken for analysis? The assumption is first made that it is the pure sesquioxide of iron. It is then seen that it contains  $\frac{112 + 100}{160}$  or 70% Fe. As the final

step in the determination is the oxidation of the ferrous to the ferric salt by means of a standard solution of  $\text{KMnO}_4$ , 1 ml. of which = 0.005 gm. Fe and as the volume of this solution is to be about 20 ml. to avoid errors in taking burette readings, it follows that if we start with 1 gm. ore we shall be using .7/.005 or 140 ml. of the  $\text{KMnO}_4$  solution. This means that when we use a 50 ml. burette, it will have to be refilled at least 3 times before finishing a determination. Ordinarily the weight of ore taken should be such that no more than one buretteful of the standard solution is required. Hence the weight of ore will be 20/140 of 1 gm. i.e., 0.14 gm. . This weight will be suitable when we are dealing with pure ferric oxide; but in practice we have to handle ores ranging from 40% to 68% Fe. To cover the cases of all the commercial grade ores, a convenient weight to take will be 0.3 gm. of the material. It cannot be too much emphasized that a calculation of this nature should precede the starting of every quantitative exercise. Omission to do this will, besides involving loss of time, and waste of reagents, lead to inaccuracy of results.

**Procedure :—***Step 1.* Weigh out a .5 gm. sample of the ore into a 100 ml. Jena flask, wash-bottle type, or a 250 ml. conical flask. Add 10 ml. conc. HCl and warm over a low flame for about 10 to 15 minutes. Increase the heat gradually and keep at a gentle boil

for about 10 minutes. Evaporate nearly to dryness and then add about 10 ml. of conc. HCl. Dilute with cold water to about 40 ml. . In case a 100 ml. capacity flask of the wash bottle type was used, transfer the solution to a 250 ml. conical flask.

*Step 2.* Add to the solution 6 gms. of pure granulated zinc (weigh the zinc to the nearest decigram on an ordinary balance). 20-mesh zinc powder, if available is to be preferred. Allow the reduction to proceed at the ordinary temperature first and as the vigour of reaction slows down, heat to boiling. When the reduction is complete, the resulting ferrous chloride solution will be colourless ; to make sure, the following test is applied : a drop of a solution of KCNS (potassium thiocyanate) is placed on a porcelain tile. A drop of the reduced solution, taken at the end of a glass rod, is allowed to mix with it. Separate rods or pieces of tubing should be used. Absence of red coloration indicates complete reduction. A suggestion of a reddish tinge may be ignored. The reduced solution is diluted in the conical flask to a volume of about 200 ml. with cold distilled water, 5 ml. of conc.  $\text{H}_2\text{SO}_4$  are next added to it and it is allowed to stand at room temperature till all the zinc goes into solution.

*Step 3.* The solution is now filtered through glass wool or asbestos, the filtrate being collected in a beaker of 750 ml. capacity. The conical flask is well washed with cold distilled water 3 or 4 times and the washings poured on to the glass-wool. In the absence of glass-wool or asbestos, absorbent cotton (bleached cotton wool) may be substituted.

*Step 4.* The filtrate contained in the beaker is diluted to a volume of about 600 ml. . Into it a standard solution of  $\text{KMnO}_4$  is run from a burette with *glass stop-*

cock and the solution stirred with a glass rod. The addition of  $\text{KMnO}_4$  solution is stopped when a faint pink colour persisting for about half a minute is obtained.

**Calculation** :—From the equation given above, it is clear that 2 formula weights of  $\text{KMnO}_4$  will oxidize 10 gm-atoms of Fe from the *ous* to the *ic* condition (*i. e.*) 316 gms.  $\text{KMnO}_4 = 10 \times 56$  or 560 gms. iron. If the standard solution of  $\text{KMnO}_4$  is  $5/56 \text{ N}$  and if 60.5 ml. of this solution are used up, then we have 1 litre  $5/56 \text{ N}$  will contain  $\frac{316}{10} \times 5/56$  gms.  $\text{KMnO}_4$ . 60.5 ml. of  $5/56 \text{ N}$  strength will contain  $\frac{1}{10} \times 5/56 \times \frac{60.5}{1000}$  gms.  $\text{KMnO}_4$ .

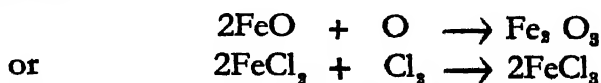
$$\begin{array}{rcl} 316 \text{ gms. } \text{KMnO}_4 = 560 \text{ gms. Fe.} \\ \frac{316 \times 5 \times 60.5}{10 \times 56 \times 1000} & & \frac{560 \times 316 \times 5 \times 60.5}{316 \times 10 \times 56 \times 1000} \\ & & \text{gms. Fe.} \end{array}$$

As a 0.5 gm. sample of ore is taken for analysis, to calculate the percentage of iron in the ore, multiply by 200.

$$\text{Percentage of iron} = \frac{5 \times 60.5}{1000} \times 200 = 60.5$$

The above calculation is lengthy and such lengthy calculations must generally be avoided. We know 1 litre  $5/56 \text{ N}$ — $\text{KMnO}_4 = 1$  litre  $5/56 \text{ N}$ —Fe.

Now a normal solution of iron will contain 56 gms. of it per litre, as will be evident from the following reaction :—



Knowing the weight of iron contained per litre of  $5/56 \text{ N}$  solution, we have to calculate the weight in 60.5 ml. and therefrom the percentage.

NOTES :—(1) To facilitate weighings to be made rather expeditiously, not damaging the balance in any way at the same time, an aluminium scoop and its counterpoise also, of aluminium, are placed one on each pan of the balance. The ore is placed on the scoop, added beingt o or removed from it by means of a stainless steel spatula and camel hair brush until it is equal to the weigh required. Very often in the technical analysis of the material now considered, it will be found that no great inaccuracy results when 0.500  $\pm$  0.001 gm. instead of 0.500 gm. is weighed out for a determination.. This should not be taken to mean that such latitude is permissible in the final weighing of a precipitate from which the % of a constituent is obtained.

(2) From the calculation it is evident that the number of ml. of  $\text{KMnO}_4$  solution of 5/56 *N* strength used up also represents the percentage of iron in the ore, when the weight taken for analysis is 0.500 gm. It will now be clear why, in preparing a standard solution of  $\text{KMnO}_4$ , we use that weight of it which will give us a solution 5/56 *N* strong. Also the reason for taking 0.500 gm. sample of ore for analysis, in preference to other weights of it, will be clear. By such procedure, the calculations become very simple and do not take time.

( In an Iron and Steel Works' Laboratory, where analysis of the same class of material is to be made every day, the procedure adopted is the one described above. Permanganate solution of any other strength may be used and any other convenient weight of ore may be taken for analysis : only the quantities of reagents will have to be suitably adjusted. )

(3) To hasten solution of the ore, boiling the same with conc.  $\text{HCl}$  very vigorously is not effective,

The acid gets weakened thereby, requiring the use of a large quantity of the acid. About 15-20 ml. conc. HCl is ample for 1 gm. ore, if gentle heat is applied for dissolving the ore.

( 4 ) When there is a residue which does not dissolve in HCl and the same contains iron, the following modification is necessary:—

Evaporate the solution of the ore in HCl to dryness. Redissolve in dil. HCl, boil and filter. Wash the residue on the filter paper free of  $\text{FeCl}_3$  by means of dil. HCl at first, and finally, with water. Call the filtrate A. Ignite the residue in a platinum crucible. Fuse the ignited residue with 2-3 gms. of fusion mixture. Extract the fusion with water, add dil. HCl until the carbonate is neutralized and some free acid is left. Boil to dissolve any residue of iron oxide. Add this solution to the filtrate A. Determine the iron from the combined filtrate as above described.

( 5 ) Reduction with zinc has the disadvantage that it reduces other salts, for example,  $\text{TiCl}_4$ , ( titanium tetrachloride ) which passes into solution, when the ore contains titanium, and when treatment of the residue in the manner described above is adopted. Such reduction leads to the registration of a higher value for iron, as the reduced  $\text{TiCl}_3$  is oxidized to  $\text{TiCl}_4$  by  $\text{KMnO}_4$ .

( 6 ) Reducing agents which do not have the above disadvantage are  $\text{H}_2\text{S}$  and  $\text{SO}_2$ . They, however, have the drawback that the removal of excess of either before proceeding with titration, takes time. In consequence, they are not generally employed in a busy Iron Works' Laboratory.

( 7 ) The reducing agent which has found most

favour in such laboratories is  $\text{SnCl}_2$ . Its use is described in Expt. 10.

( 8 ) In the case of certain ores, notably the black band ore used in England, ignition for half an hour in a platinum crucible is necessary before dissolving in  $\text{HCl}$ . Certain organic matters are thus destroyed which would otherwise cause high results.

( 9 ) The high\* results for iron, arising from any inadvertent use of excess of  $\text{HCl}$ , in solutions containing ferrous iron when they are to be titrated with potassium permanganate, can be avoided by adding 20 ml. of the following mixture to the solution ready for titration:—

Manganous sulphate crystals C. P.	90 gms.
Water	650 ml.
Sulphuric acid ( S.G. 1.84 )	175 ml.
Ortho Phosphoric acid ( S.G. 1.70 )	175 ml.

Dissolve the manganous sulphate in 150 ml. of water. Add the phosphoric acid to about 200 ml. of water. Pour the concentrated sulphuric acid into about 300 ml. of water. Pour the three solutions, in the order mentioned, into a litre bottle. Use the solution after it has stood 3-4 days. In the freshly prepared condition, it has a slight oxidizing action.

With such a solution ready to hand the reduction of ferric iron may be effected by means of  $\text{SnCl}_2$  solution in place of zinc. Further details of procedure are the same as those described in Experiment 10, (i.e.) 20 ml. of the above mixture are introduced into the solution which has been got ready for titration by reduction with  $\text{SnCl}_2$  and the addition of  $\text{HgCl}_2$ . The above reagent is referred to sometimes as the 'Zimmermann-Reinhardt Reagent'.



### A few explanations as to the details of procedure :—

Measured quantities of acid are used for two reasons: first, in most cases large quantities of them will interfere with the accuracy of the determination; secondly, all waste should be avoided. In the determination in question, 10 ml. of conc. HCl are used to start with. A larger volume of the acid is unnecessary to bring the weight of ore taken into solution; also the larger volume will take time to get reduced in bulk. The second addition of about 10 ml. conc. HCl is made to have sufficient acid in the flask for the subsequent reactions: namely, the reduction with zinc and the final titration with  $\text{KMnO}_4$ . If too large a volume of HCl were used at this stage, it would interfere with the final titration in the following manner:—



Chlorine will be evolved and the volume of  $\text{KMnO}_4$  being higher, a higher percentage of iron will be returned.

The object of adding 5 ml. conc  $\text{H}_2\text{SO}_4$  is to reduce to a minimum the above reaction. It must be remembered that permanganate titrations when made with solutions containing HCl cause a slight inaccuracy because of the above reaction. The presence of  $\text{H}_2\text{SO}_4$  tends to reduce the error thus caused to a minimum.

It is necessary to take a weighed amount of zinc because it contains small quantities of iron which must be determined and allowed for. As the quantity of iron present in it is small and consumes about 0.2 to 0.5 ml. of the standard  $\text{KMnO}_4$  when 6 gms. of zinc are used, it is enough if the zinc is weighed to the nearest decigram.

Though the reduction of iron to the 'ous' condition is complete before all the zinc is dissolved, it is necessary to wait for all the zinc to dissolve, as a blank determination for iron in the zinc has to be run, using the same weight of zinc and the same volumes of acid as were used in the analysis of the ore.

The reduced solution is filtered through glass-wool or asbestos because absorbent cotton filter, if used, will register a somewhat higher percentage of iron due to the oxidation of any cotton fibre that might pass through, by the permanganate. In technical analysis, the use of cotton is not so very objectionable. Filter-paper, if used, will consume much time for filtration. The reason why the reduced solution is filtered at all is this: zinc contains in addition to iron, arsenic, lead, etc. These do not go into solution completely. They consume  $\text{KMnO}_4$  through indirect action and will register a higher percentage for iron. The amount of permanganate consumed becomes variable when the ore treated contains also lead, arsenic, etc. and a blank determination for these impurities in the ore cannot be made. Hence, the necessity for filtering off the residue left.

Large dilution to a volume of 600–700 ml. is necessary to reduce the action between  $\text{HCl}$  and  $\text{KMnO}_4$  to a minimum and to get a fairly sharp end-point.

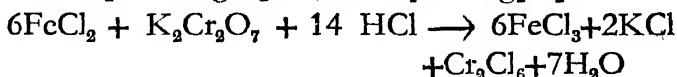
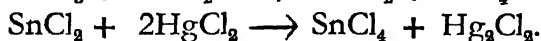
## EXPERIMENT 10

### Determination of Iron in Iron ore making use of Standard Potassium Dichromate solution.

**Principle :** The ore if hematite is brought into solution in  $\text{HCl}$ ; if it is pyritic, in aqua regia; evaporated to fumes with  $\text{H}_2\text{SO}_4$  and redissolved in conc.  $\text{HCl}$ . The *ic* chloride thus obtained is reduced while boiling hot to the *ous* condition by means of stannous chloride

solution. The reduced colourless solution is cooled, treated with a solution of  $\text{HgCl}_2$  to remove excess of stannous chloride and then titrated with standard  $\text{K}_2\text{Cr}_2\text{O}_7$  using potassium ferricyanide as external indicator.

The essential reactions involved are given below :—



### Solutions required :

#### 1. Solution of Potassium Dichromate :—

Calculate the weight of dichromate necessary to get a litre of the solution 5/56 *N* strong. This will be 4.39 gms. This will be clear from the following :—

One formula weight of  $\text{K}_2\text{Cr}_2\text{O}_7$  has 3 available gm atoms of oxygen for oxidation. It splits into  $\text{K}_2\text{O}$ ,  $\text{Cr}_2\text{O}_3$  and 3 O in the process. Hence a normal solution of dichromate will contain  $\frac{\text{K}_2\text{Cr}_2\text{O}_7}{6}$  or  $\frac{294.5}{6}$  or 49.083 gms.

per litre. Dichromate solution of 5/56 *N* strength is chosen for the reason that 1 ml. of this solution corresponds to 0.005 gm. iron and when 0.5 gm. of a sample of iron ore is taken for analysis, the number of ml. of the dichromate solution used will give the percentage of iron directly.

#### 2. Stannous chloride solution :—

Dissolve 50 gms. stannous chloride in 200 ml. conc. HCl. Dilute with water to 1 litre. Preserve by adding a few pieces of granulated tin.  $\text{SnCl}_4$  formed by atmospheric oxidation is thereby reduced to  $\text{SnCl}_2$ , and the reagent thus kept intact.

#### 3. Mercuric chloride solution :—

A saturated solution in water at the laboratory temperature..

#### Potassium ferricyanide indicator :—

Dissolve a piece half as big as a pea in 50 ml. distilled water. Wash a crystal of the above size in distilled water by holding it between the fingers to remove traces of ferrocyanide on the surface of the crystal. Dissolve the crystal thus washed in 50 ml. water.

**Procedure:**—Weigh exactly 0.5 gm. sample of the hematite ore into a 250 ml. conical flask. Add 10 ml. conc. HCl and heat over a low flame for a few minutes and then increase the heat gradually. Keep at a gentle boil until nearly evaporated to dryness. Add 8 ml more. conc. HCl. Dilute to about 40 ml. with cold distilled water and then heat to boiling. Take off the burner and add stannous chloride solution from a dropping bottle, drop by drop, shaking the conical flask all the while until the red colour is completely discharged. Add a few drops more. Cool to the Lab. Temp. by running cold water from the tap on to the outside of the flask, add 10 ml.  $\text{HgCl}_2$  and dilute to 200 ml. with cold distilled water. Run potassium dichromate solution into the reduced solution after transferring it to a beaker of 500 ml. capacity. (To facilitate thorough mixing during titration, the reduced iron solution is transferred from the conical flask to a beaker). Add 20 ml. of the dichromate at first, stirring well with a rubber-tipped glass rod. Take out a drop from the beaker and allow it to mix with a drop of potassium ferricyanide solution (freshly prepared) on a spot plate. Use a separate piece of glass tubing for transfer of ferricyanide to the spotting plate. If a blue colour develops, all the *ous* iron has not been oxidized to the *ic* condition. Continue the addition of the dichromate, testing between 5 ml. additions, using a fresh drop of the indicator for each test, and afterwards between 1 or 2 ml. additions, as suggested by the less and less intense blue coloration. The end-point is reached when

immediately on the addition of a drop from the titrating beaker, there is no blue colour developed. If the dichromate solution is of the strength prescribed, the number of ml. of the dichromate solution used registers the percentage of iron in the ore. If it is of any other strength, say,  $N/10$ , the iron percentage may be calculated as follows:—

$$\begin{array}{ll}
 1 \text{ ml. of } 5/56 \text{ } N \text{ corresponds to } 0.005 \text{ gm. Fe} & \\
 n \text{ ml. } N/10 & \text{,,} \quad \frac{.005 \times 56 \times n}{5 \times 10} \text{ gm. Fe} \\
 .5 \text{ gm. ore contains } & \frac{.005 \times 56 \times n}{56} \text{ gm Fe.} \\
 100 \text{ gms. } & \text{,,} \quad \frac{.005 \times 56 \times n \times 200}{50} \text{ gm. Fe.}
 \end{array}$$

Notes:—( 1 ) This method possesses a distinct advantage over the reduction with zinc in that the reduction is completed in a minute or two. But the titration with dichromate takes more time than the titration with permanganate. Also in this case, the use of an external indicator is unavoidable. In Iron and Steel Works' Laboratories where a number of analyses of the same class of ore has to be made, reduction is effected by means of stannous chloride and the subsequent titration carried out with dichromate solution. As there is always a danger of overstepping the end point by the method of titration described above, the following modification may, with advantage, be made :

Reserve about 50 ml. of the solution, which is ready for titration, in a small beaker ; titrate the main portion until the end-point is slightly passed, then transfer some of the reserve solution and continue the titration cautiously until the end-point is nearly reached. Then mix with the rest of the reserve solution and

cautiously add until the end-point is just reached. Titration with  $\text{KMnO}_4$  of solution containing  $\text{HCl}$ , gives rise to somewhat higher results while that with  $\text{K}_2\text{Cr}_2\text{O}_7$  is not affected at all ; as a matter of fact, whenever a hydrochloric acid solution of ferrous iron is to be titrated, the latter oxidant is preferred.

(2) In case the residue on dissolving the ore in  $\text{HCl}$  contains iron, it is necessary to filter off the solution, ignite the residue, fuse with fusion mixture, dissolve the fused mass in  $\text{HCl}$ , add the solution to the original filtrate and proceed with reduction with  $\text{SnCl}_2$  solution and titration with  $0.1\text{ N K}_2\text{Cr}_2\text{O}_7$ , using the external indicator. The details are shown under 'Notes' para 4, Expt. 9, page 58.

(3) In technical practice, the usual procedure is to make as many determinations as possible from one and the same weighing of the sample of ore, metal or alloy. The determination of iron may be carried out along with that of  $\text{SiO}_2$ . This procedure helps to save time and reagents. Apart from such considerations, when the quantity of material available for analysis is small or limited, determination of as many constituents as possible from one weighing is a necessity.

(4) In recent years, an internal indicator has been introduced for the titration of ferrous iron with standard dichromate. This indicator is made as follows :—

1 gm. diphenylamine is added to 100 ml. conc.  $\text{H}_2\text{SO}_4$  contained in a dropping bottle. 2-3 drops of the indicator will suffice for each titration. It gives an intense violet-blue colour when the ferrous iron has been completely oxidized and one drop of  $0.1\text{ N K}_2\text{Cr}_2\text{O}_7$  is in excess. The deep violet-blue colour can be destroyed by introducing excess of a standard ferrous ammonium sulphate solution, so that even if the end-point is

considerably passed, when adding the dichromate, it is possible to hit it off exactly by introduction of excess of 0.1 N ferrous ammonium sulphate and finishing off carefully with 0.1 N  $K_2Cr_2O_7$ .

The sharpness of the end point is improved by the addition of 20 ml. of the following mixture to the solution which is ready for titration :—

Sulphuric acid (S. G. 1.84) 150 ml.

Ortho phosphoric acid (S. G. 1.70) 150 ml.

Water to make 1000 ml.

Add the sulphuric acid to about 300 ml. water contained in a flask of about 1000 ml. capacity. Pour into this the phosphoric acid and add water to make a total volume of about 1000 ml. Mix thoroughly.

The indicator solution retains its usefulness even when it turns brown.

#### **A few explanations on the procedure :—**

Recall the remarks made in connection with the bringing of the ore into solution in the determination of iron using  $KMnO_4$  standard solution. The stannous chloride is added from a *dropping bottle* to the *boiling hot* ferric chloride solution, as a large excess of  $SnCl_2$  is to be avoided, and as the reduction is quickest when the solution is boiling hot.  $FeCl_3$  is colourless. So the addition of  $SnCl_2$  is stopped when the red or yellow colour of  $FeCl_3$  is completely discharged. To have a slight excess, thus making sure that the reduction is complete, a few drops more of  $SnCl_2$  are added. The solution is quickly cooled, as, otherwise, the reduced solution will be oxidized by the oxygen in the air. To the cold solution, 10 ml.  $HgCl_2$  are added; this volume is enough to react with the excess of  $SnCl_2$ . An excess of  $HgCl_2$  does no harm; but a deficiency of it will register a higher percentage for iron, as in this

case, all the  $\text{SnCl}_2$  will not be removed and the latter will consume dichromate solution, being oxidized to  $\text{SnCl}_4$ . The addition of  $\text{HgCl}_2$  is made to the *cold* and not to the hot reduced solution because in the latter case, a precipitate of  $\text{Hg}$ , in a very finely divided condition, will be obtained which will also be oxidized by the dichromate, thereby yielding a higher percentage for iron. A fair dilution of the reduced solution is necessary in order to minimise the error caused by having to take out test-drops.

The reaction leading to the separation of finely divided  $\text{Hg}$  is as follows :—



### EXPERIMENT 11.

#### **Analysis of Limestone, dolomite, magnesite :—**

Limestone and dolomite are used as fluxes in the Iron Blast Furnace. They are also used in the calcined condition as fluxes in steel making by the basic open hearth process. Magnesite is the raw material for the manufacture of magnesite bricks used in the construction of basic open hearth furnaces.

Standard solution required :—0.1 N  $\text{KMnO}_4$ .

#### **Principle of method :—**

The limestone is dissolved in  $\text{HCl}$  when  $\text{SiO}_2$  separates as a residue. This is filtered off. The filtrate contains  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{CaCl}_2$  and  $\text{MgCl}_2$ . The two first are precipitated as hydroxides by ammonia, filtered off, ignited and weighed. By treatment with  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ ,  $\text{CaCl}_2$  yields  $\text{CaC}_2\text{O}_4$  as a precipitate when the medium is slightly ammoniacal. The precipitate is filtered off, dissolved in sulphuric acid and titrated with 0.1 N  $\text{KMnO}_4$ . See Expt. 8 for the titration reaction.  $\text{MgCl}_2$  on treatment with  $(\text{NH}_4)_2$



$\text{HPO}_4$  and ammonia yields  $\text{MgNH}_4\text{PO}_4$ . This is ignited and weighed.

Obtain a dry sample as follows:-Spread in a thin layer about 3-5 gms. of the powdered material on a 3" watch glass. Heat in an air oven, Fig. 3 a (gas-heated) or 3 b (electrically-heated) at  $105^\circ\text{C}$ . for an hour. Cool in a desiccator.

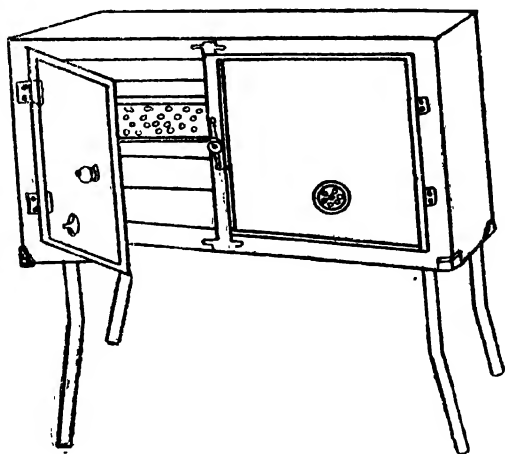


Fig. 3 a



Fig. 3 b

**Determination of  $\text{SiO}_2$  :—**Weigh 0.500 gm. of the dry sample into a 200 ml. beaker covered with a cover-glass. Add a mixture of 10 ml. of water and 10 ml. of 1.1.s.g. HCl, gradually. When the vigorous effervescence is over, add a drop or two of conc.  $\text{HNO}_3$  and evaporate to dryness on the hot plate. Continue heating at  $110^\circ - 120^\circ\text{C}$ . for half an hour to dehydrate the silicic acid. Cool; add 10 ml. of HCl S.G.1.1 and 10 ml. of water; gently boil and filter off the residue through a 9 cm. filter paper; rinse the beaker five or six times using about 10 ml. of hot water each time; transfer the residue on to the filter paper and wash the filter paper thoroughly with hot water two or three times more, each time allowing the liquid completely to drain. Dry the filter-paper in an air oven. Spread on a clean and dry watch glass and let stand in the oven for half of an hour. Remove from the oven, transfer to a silica, porcelain or platinum crucible, ignite first over a Bunsen burner and then over a blast lamp; cool in a desiccator and weigh. The weight multiplied by 200 gives the percentage of 'Insoluble Matter'. If  $\text{SiO}_2$  is required, the ignition must be conducted in a platinum crucible, the cooled mass weighed with the crucible, the residue hydrofluorised ( See Expt. 56. ) and then ignited, cooled and weighed. The difference between the two weighings gives the weight of  $\text{SiO}_2$  on 0.5 gm. sample from which the percentage is calculated. In ordinary technical practice, it is enough if the 'Insoluble Matter' is reported.

**Determination of  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$  :—**To the filtrate from the 'Insoluble Matter', 2 gms. of solid ammonium chloride are added, the volume of the filtrate made to about 150 ml. and ammonium hydroxide ( S. G. 0.96 ) is added until the liquid smells of ammonia. The liquid with the precipitate is boiled for two or three minutes.

At the end of this time, the smell of ammonia should still be noticeable ; if there is no smell of it, run more of the reagent by means of a glass rod into the boiling liquid. Boil until there is a faint smell of ammonia. The precipitate is allowed to settle for a few minutes, then filtered off and washed free of chloride, ( test ? ) dried, ignited in a porcelain crucible over a Bunsen burner, cooled in a desiccator and weighed. The weight obtained multiplied by 200 gives the percentage of  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ .

To obtain the amount of each constituent separately, either of the two following methods designated as A and B may be adopted.

**Solutions required:—**

( 1 ) 0.02 N  $\text{KMnO}_4$ . Dissolve 0.65 gm. of the salt in 1 litre of water and standardize against pure  $\text{Na}_2\text{C}_2\text{O}_4$  as in Experiment 8, or, dilute 20 ml. 0.1 N  $\text{KMnO}_4$  prepared in Experiment 8 to 100 ml. exactly in a 100 ml. measuring flask, with water. Mix and use. The former is the more correct procedure.

( 2 ) Stannous chloride solution:—5 ml. of the solution prepared in Experiment 10, page 62, is diluted to about 25 ml. with dil. HCl of 1.1. S.G.

( 3 ) Mercuric chloride solution:—the same as in Expt. 10.

( 4 ) The Zimmermann-Reinhardt Reagent: See para 9, Notes, Expt. 9, page 59.

**Method 'A':**—The ignited residue is transferred, after weighing, to a conical flask ( 100 ml. capacity ) ; dissolved in conc. HCl ( 10 ml. ) with the aid of a few drops of  $\text{SnCl}_2$  and gentle heat for about an hour. In about this time, the residue goes into solution completely. The hot solution containing Fe and Al in the form of the chlorides in trivalent condition is reduced

with  $\text{SnCl}_2$  so that the *ic* iron changes to the *ous* iron. This solution is cooled ; treated with 5-10 ml. of  $\text{HgCl}_2$  and titrated with standard  $\text{KMnO}_4$  solution in a porcelain basin of 1 litre capacity containing about 500 ml. of distilled water to which has been added 30 ml. of  $\text{MnSO}_4$  solution (the Zimmermann-Reinhardt Reagent). The solution helps to give accurate results for iron when the solution contains some free hydrochloric acid and the permanganate titration is adopted. From the number of ml. of the standard  $\text{KMnO}_4$  used, the amount of iron is calculated. This is changed to  $\text{Fe}_2\text{O}_3$ . This weight is deducted from the combined weight of  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ . Thus  $\text{Al}_2\text{O}_3$  is obtained separately.

#### NOTES:--

( 1 ) Ignited iron oxide from ferric hydroxide precipitate does not dissolve readily in conc.  $\text{HCl}$ . The addition of a few drops of  $\text{SnCl}_2$  hastens solution.

( 2 ) A blank using the same volume of reagents and distilled water as in an actual run should be made. The number of ml.  $\text{KMnO}_4$  used to give a pink colour of the same intensity as in the sample run should be deducted from the number of ml. for the assay and the calculation of  $\text{Fe}_2\text{O}_3$  then made.

( 3 ) When the amount of the constituent determined is small, it is the usual practice to make the standard solution very weak, thereby avoiding errors in burette readings, necessarily arising when only 0.5 or 1 ml. of the stronger standard is consumed.

(4) The use of dichromate standard solution is not possible when percentages of iron smaller than 5, as in the present case, are being determined. The solution of iron is so weak that the reaction with  $\text{K}_3\text{Fe}(\text{CN})_6$  does not give a sharp end point.

(5) The diphenylamine indicator may be used when using  $N/30$ - $N/50$  permanganate solutions.

**Method B :—**Weigh 1 gm. of the sample into a 200 ml. beaker. Add a mixture of 10 ml. HCl of S.G. 1.1 and 50 ml. water. Bring into solution by gentle boiling. Reduce with  $\text{SnCl}_2$  and proceed as in the determination of iron in iron ore using the permanganate method of titration. From the percentage of  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ , deduct the % of  $\text{Fe}_2\text{O}_3$  to get the % of  $\text{Al}_2\text{O}_3$ . For a colorimetric method for Fe, see Experiment 52.

**Determination of CaO :—**To the filtrate from the hydroxides of aluminium and iron, add 3-4 gms. of solid ammonium chloride. Raise to a boil. Add 30 ml. of a saturated, boiling hot solution of ammonium oxalate. Continue to boil for a minute or two longer. Allow the precipitate to settle for one hour at  $90^\circ$ - $100^\circ\text{C}$ . Filter off the precipitate of calcium oxalate; wash it free of the precipitant (i. e. ammonium oxalate) with boiling hot distilled water. Test the filtrate by running about 5 ml. from the funnel during washing into a test tube; acidify with about 10 drops of  $6N\text{-H}_2\text{SO}_4$ , raise to a boil; add 1 or 2 drops of the standard  $\text{KMnO}_4$  solution. If the pink colour does not persist, the precipitate is not free from ammonium oxalate. When free, puncture a hole in the filter paper with a pointed glass rod and wash down the precipitate into a 600 ml. beaker with hot water; dissolve it by pouring through the filter paper hot dilute  $\text{H}_2\text{SO}_4$  (about 10 ml. of  $6N$ -acid). Wash the filter-paper a few times with hot water, collecting the water in the same 600 ml. beaker. Raise the solution of calcium oxalate in dil.  $\text{H}_2\text{SO}_4$  to about  $70^\circ\text{C}$ . and titrate with standard  $\text{KMnO}_4$ . The

solution of  $\text{KMnO}_4$  used in iron determination in Expt. 9 may be used.

1 ml. of  $\text{KMnO}_4$  = 0.005 gm. Fe.

1 ml. of the same = 0.0025 gm.  $\text{CaO}$ .

The value of  $\text{KMnO}_4$  in terms of  $\text{CaO}$  is obtained by multiplying the iron value by 0.5. From the following, the above will become evident :—

1 litre  $N/10 \text{ KMnO}_4 = 1 \text{ litre } N/10 \text{ CaC}_2\text{O}_4 = 1 \text{ litre } N/10 \text{ CaO}$

1000 ml. of  $N/10 \text{ KMnO}_4 = 56/20$  or 2.8 gms.  $\text{CaO}$

1000 ml. of  $N/10 \text{ KMnO}_4 = 56/10$  or 5.6 gms. Fe.

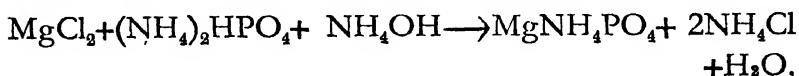
Alternatively, the precipitate of  $\text{CaC}_2\text{O}_4$  may be ignited in a platinum crucible to  $\text{CaO}$  and the oxide weighed. Ignition should be repeated until two consecutive weighings agree. Owing to the rapid absorption of  $\text{CO}_2$  by  $\text{CaO}$  from the air, special precaution should be taken to leave, both in the desiccator and in the balance case, a small quantity of soda-lime in a glass tray to absorb  $\text{CO}_2$  present. The titration method is to be preferred and is followed in Works' Laboratories.

**Determination of  $\text{MgO}$  :—**Reduce the bulk of the filtrate to a volume of 300 ml. by evaporating in a large-size basin, after adding 2-3 ml. conc.  $\text{HCl}$ . When the solution is boiling hot, add 20 ml. of a saturated solution of  $(\text{NH}_4)_2\text{HPO}_4$ . Stir vigorously and introduce 100 ml. of 0.96 S.G. ammonia, continuing the stirring all the while. Let stand 2 hours or, until cold, and filter. Wash the precipitate free of ammonium chloride with 2.5% ammonia-water, which is obtained by mixing one volume of ammonia of s.g. 0.88 with nine volumes of water. Transfer the precipitate with the filter-paper to a porcelain crucible. Heat slowly so that the filter

paper is dried. Gradually increase the heat to char it. Continue to raise the heat so that the black mass is completely oxidized. At this stage, maintain the full heat of a Teclu burner or a blast lamp for half an hour. Cool and weigh. From the weight of the pyro-phosphate of magnesium, calculate the percentage of magnesia.

NOTES :—

(1) The reaction that takes place when to a slightly acid solution of a magnesium salt, ammonium phosphate followed by  $\text{NH}_4\text{OH}$  is added is as follows :—



When the precipitate of  $\text{MgNH}_4\text{PO}_4$  is strongly ignited, it decomposes as follows :—



When the precipitation of  $\text{MgNH}_4\text{PO}_4$  takes place in a cold solution, the precipitate must be allowed to settle for a period of 12 hours before it is filtered off. In technical practice where many samples have to be analysed, the precipitation is made in the evening, the precipitate allowed to stand overnight, filtered off in the morning and then ignited. The precipitate, when formed from a hot solution, can be filtered off after standing for only two hours, as it is coarsely crystalline when precipitated hot and settles down quickly.

(2) The ignition of the precipitate to convert it into the pyrophosphate takes a long time, more than an hour from the start. Even after such prolonged heating, it does not sometimes become perfectly white. This is due partly to traces of organic matter in the reagents used and partly to forcing up the rate of heating during the charring of the paper. The more

gradual and the more complete the charring, the whiter is the pyrophosphate obtained.

**Modification due to J. O. Handy :—**Equally accurate results have been obtained by this method. It has the advantage of simplicity and can be adopted in localities where a gas supply for heating purposes is not available.

**The Method:—**Dry the filter paper with the precipitate of  $\text{MgNH}_4\text{PO}_4$  in an air-oven at a temperature of  $50\text{--}60^\circ\text{C}$ . for 15 minutes. Place the dry filter with the residue in a dry beaker, add a measured excess of  $N/10 \text{ H}_2\text{SO}_4$  and stir until dissolved. Add two or three drops of 0.1% alcoholic solution of methyl orange. Dilute to 100 ml. with water, add from a burette  $N/10 \text{ NaOH}$  until a distinct yellow colour free from all suggestion of pink is obtained.

1 ml.  $N/10 \text{ H}_2\text{SO}_4 = 0.002 \text{ gm. MgO}$ .

(3) **In the case of dolomite** in which  $\text{CaO}$  and  $\text{MgO}$  are present in nearly equal amounts, and in the case of magnesite where  $\text{Mg}$  is present to the extent of about 45% and  $\text{CaO}$  only about 2%, the precipitate of  $\text{CaC}_2\text{O}_4$  obtained as above described will be contaminated with  $\text{MgC}_2\text{O}_4$ . To free the former from the latter, redissolve the precipitate in 3 to 5 ml. of  $6N\text{--HCl}$ , make slightly ammoniacal, dilute to a volume of 50-75 ml. with distilled water and again treat with 5 ml. of a saturated solution of ammonium oxalate, both being boiling hot. Let stand for half an hour. Filter. Add the filtrate from the calcium oxalate to the original filtrate and from the combined filtrates determine  $\text{MgO}$  as already described. If  $\text{CaC}_2\text{O}_4$  is not reprecipitated in the manner described, the results for  $\text{CaO}$  will run high while those for  $\text{MgO}$  will run low.



The double precipitation may be dispensed with in the case of dolomite when the calcium is precipitated in the manner described below:—

To the boiling solution containing calcium and magnesium chlorides not exceeding 11 gm. and not much exceeding a volume of 300 ml., add 1 gm. oxalic acid and slowly neutralize by means of *N*-ammonia (1 volume of ammonia s. g. 0.88 diluted with 15-16 volumes of water). Allow to stand for an hour and filter. Determine the lime as described above by titration with standard  $\text{KMnO}_4$  and determine  $\text{MgO}$  in the filtrate.

In the case of magnesite, a reprecipitation of  $\text{CaC}_2\text{O}_4$  is necessary.

**Loss on ignition:**—Ignite 1 gm. of the sample in a platinum crucible covered with lid, over an ordinary burner for about 5 minutes and then over a blast-lamp for about 20-30 minutes. Cool in a desiccator and weigh.

The lower the percentages of 'Insoluble matter',  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ , the more valuable the materials are as fluxes.

See CHAPTER I, page 18 for a note on the appropriate grade of filter paper for filtering off precipitates of different particle-size.

## EXPERIMENT 12.

### Analysis of Portland Cement.

**Introductory:**—The British Engineering Standards Association has laid down specifications regarding the composition of portland cement as in the case of other materials of construction. The manufacturer has to control the process so that the material will conform to

those specifications. As a check on the figures of analysis given by the manufacturer, the buyer or, the government on his behalf, carries out the analysis. The method adopted is very similar to the one for limestone given in the preceding experiment, with a few modifications necessitated by the presence in cement of certain constituents in larger amounts than in limestone. Portland cement is essentially a mixture of the silicates of calcium and magnesium with aluminate of calcium. It contains a small amount of  $\text{CaSO}_4$  introduced during the grinding of 'clinker' with a view to regulate the time of setting. The following are determined:—

$\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ , Loss on Ignition and  $\text{SO}_3$ . Alkalies are only occasionally determined and for the method of determining them, see Experiment 76.

### Principle :—

The material is treated with  $\text{HCl}$  when  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{CaCl}_2$  and  $\text{MgCl}_2$  are obtained in solution,  $\text{SiO}_2$  separating as a residue. This is filtered off, ignited and weighed.  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{MgO}$  are determined from the filtrate.

$\text{SO}_3$  is determined separately by weighing out a fresh quantity of the sample.

### Procedure:—

Weigh into a 250 ml. porcelain casserole 0.500 gm. of the cement. Add 40 ml. water. Boil on a hot plate. When boiling, add dil.  $\text{HCl}$  of s. g. 1.1 in small quantities at a time, the total volume of acid so added being about 20 ml. . If any lump forms, break it up with the flattened end of a stirring rod. Cover the casserole with a watch glass and continue heating on the hot plate 15 minutes longer. Rinse the bottom of the watch glass with water, collecting the rinsing in the casserole. Insert a glass triangle between the casserole and the watch

glass and evaporate to dryness on a water bath. Heat the dry mass for 1 hour in an air oven kept at  $120^{\circ}\text{C}$ .

### Determination of $\text{SiO}_2$ :-

Moisten the residue with 10 ml. dil. HCl of 1.1 s. g. Warm slightly and add 150 ml. water. Keep at the boiling temperature for 10 minutes. Filter into No. 7 beaker ( 400 ml. ) Wash alternately with very dilute HCl and hot water until the residue on the filter paper is free from iron. Finally wash it free of chloride with hot water. Make sure that it is free from chloride by testing as follows :— Collect about 5 ml. in a test tube and add a few drops of  $\text{AgNO}_3$  solution of 2% strength. If there is no turbidity, the residue is free from chloride. This test should be carried out only after 3-4 washings, as, if made earlier, some Ca or Mg may be lost and the results for these turn out a little low.

Transfer the residue with the filter paper to a porcelain or platinum crucible, dry at a low heat, gradually raise the temperature and finally ignite over a blast lamp to constant weight. Report as  $\text{SiO}_2$ .

### $\text{Fe}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$ .

To the filtrate add ammonia of 0.96 s. g. until a slight excess is present, boil until only a faint smell of ammonia is noticeable. Filter off the hydroxides of iron and aluminium. Collect the filtrate in a 600 ml. beaker. Wash the filter paper and residue only twice. Acidify the filtrate and concentrate it by heating on the hot plate. In the meantime, redissolve the hydroxides on the filter paper by pouring on to them a boiling hot mixture of 5 ml. of dil.  $\text{HNO}_3$  of s. g. 1.2 diluted with 20 ml. water. Receive the solution in a 200 ml. beaker. Pour solution on to the filter paper a second time and collect the filtrate in a second beaker.

Repeat this operation until there is no more residue on the filter paper. Wash thoroughly with water. Boil to dissolve the precipitate. Dilute to 150 ml. with water. Add ammonia of s. g. 0.96 to the solution of  $\text{Fe}(\text{NO}_3)_3$  and  $\text{Al}(\text{NO}_3)_3$  until it smells of ammonia, boil until there is only a faint smell of ammonia, filter through the same filter paper as before, after stirring in one filter paper of 9 cm. dia. torn into bits. Collect the filtrate in the beaker containing the original filtrate which was allowed to concentrate by boiling. Remove the beaker to a hot plate. Wash the residue until free from chloride, collecting the washings in a second beaker. Reject the washings. Ignite the paper with the residue in a porcelain crucible. Cool and weigh as  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ . To determine each separately, proceed exactly as in Experiment 11, Method A. On account of the extra paper introduced, the ignited residue is more easily dissolved in  $\text{HCl}$ , making the determination accurate.

NOTES :—

(1) To bring the cement into solution, it is necessary to boil it with water and add the acid gradually. Addition of acid in bulk at room temperature leads to the formation of a layer of silicic acid round the particles of cement, which layer is not penetrated by further quantities of  $\text{HCl}$ . Thus the cement is only superficially attacked. To prevent this, it is necessary to proceed in the manner indicated.

(2) Filtering off the  $\text{SiO}_2$ , baking a second time with  $\text{HCl}$  to recover small amounts of  $\text{SiO}_2$  in the filtrate is not generally adopted in routine analysis of cement, though such a procedure is obligatory in analysing fireclays and other materials high in silica.

(3) A temperature much higher than  $120^\circ\text{C}$ . for baking will lead to the combination of basic magnesium

chloride with silicic acid which will not be readily dissolved by dil. HCl during the subsequent treatment.

(4) The hydroxides of iron and aluminium occlude small quantities of Ca and Mg salts, making the results for Fe-Al oxides run high and those for Ca and Mg oxides run low. To separate these, the hydroxides should be redissolved in acid and again precipitated by adding ammonia. Nitric acid is preferred to HCl for redissolving the precipitate, as thereby the washing of the precipitates, again formed by adding ammonia, free from chlorides is more easily effected. Chlorides, if present in the precipitates of  $\text{Fe}(\text{OH})_3$  and  $\text{Al}(\text{OH})_3$ , will cause a slight loss of these metals during ignition of the respective chlorides. Nitrates, even if they are not completely removed by washing, do not form any volatile compounds with  $\text{Fe}(\text{OH})_3$  during ignition.

The extent to which a precipitate will adsorb or occlude substances in solution depends upon the concentration of the solution, temperature, etc. Refer to page 419 of 'A class Book of Physical Chemistry' by Lowry and Sugden, 1927 Edition, Macmillan & Co., for the phenomenon of adsorption. The double precipitation minimises losses by adsorption.

### **Determination of CaO :—**

Make the combined filtrate from the hydroxides of aluminium and iron slightly acid with  $\text{HNO}_3$  and concentrate to about 300 ml. Add 1 gm. oxalic acid followed by dilute ammonium hydroxide (1 volume 0.88 s.g. ammonia and 15-16 volumes of water) until the liquid smells slightly of ammonia. Introduce the ammonia little by little. About 5 minutes taken in adding the ammonia helps the formation of the precipitate of calcium oxalate in a condition which is not contaminated by  $\text{MgC}_2\text{O}_4$  and at the same time the particles are of such a

size that they will not pass through the filter paper during the subsequent filtration. From this point, proceed exactly as in Experiment 11 until the titration with 0.1 N  $\text{KMnO}_4$  for  $\text{CaO}$  is finished.

### Determination of $\text{MgO}$ :—

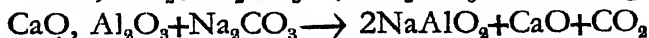
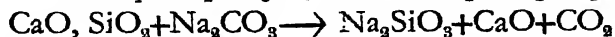
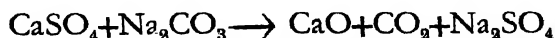
From the filtrate from  $\text{CaC}_2\text{O}_4$ , determine  $\text{MgO}$  exactly as in Experiment 11.

### Loss on Ignition:—

Heat 0.500 gm. of the cement for five minutes in a platinum crucible covered with lid over a low flame and then strongly over a blast lamp for 15 minutes.

### Determination of $\text{SO}_3$ :—

**Principle:**—When the cement is fused in an iron crucible with a mixture of  $\text{Na}_2\text{O}_2$  and  $\text{Na}_2\text{CO}_3$ , the  $\text{CaSO}_4$  present in it is transformed into  $\text{Na}_2\text{SO}_4$ , sodium silicate and aluminate being formed at the same time.  $\text{Ca}$  and  $\text{Mg}$  are changed to oxides. When the fused mass is extracted with water and the extract filtered, the filtrate contains all the sulphur as  $\text{Na}_2\text{SO}_4$ . It also contains  $\text{Na}_2\text{SiO}_3$  and  $\text{NaAlO}_2$ . To remove the  $\text{SiO}_2$ , the filtrate is acidified with  $\text{HCl}$ , evaporated to dryness, the dry mass redissolved in  $\text{HCl}$  and the separated  $\text{SiO}_2$  filtered off. From the filtrate, the sulphur is precipitated as  $\text{BaSO}_4$  by the addition of  $\text{BaCl}_2$ . The reactions during fusion are:—



### Procedure:—

Introduce about 2 gms. of the peroxide into an iron crucible. Weigh into it exactly 0.5 gm. sample of cement. Introduce about 2 gms. of  $\text{Na}_2\text{CO}_3$ . Mix thoroughly by means of a glass rod. Brush off anything

adhering to the rod, into the crucible. This step of stirring with a glass rod must be omitted during the rainy season. Heat over a Teclu burner until the mass is well fused. About 15 minutes will do. Cool. Introduce the crucible into a beaker containing about 120 ml. hot water. Lift the crucible off the surface of water by means of a pair of tongs, and rinse it well with water. Examine the bottom of the crucible. If any residue is still sticking, add hot water and stir with a rod. Transfer the solution to the beaker. Repeat until all the residue is removed. Filter off the undissolved matter consisting of  $\text{Fe}_2\text{O}_3$  and  $\text{MgO}$ . Make the filtrate acid with  $\text{HCl}$ . Evaporate on the water bath to dryness. Redissolve the dry mass in 5 ml. dil.  $\text{HCl}$  of s. g. 1.1. Dilute to 200 ml. and filter. Wash the residue 5 or 6 times with water. Boil the filtrate. Add to it, when boiling hot, 10 ml. of a 10% solution of  $\text{BaCl}_2$  which is also boiling hot. Continue boiling for a minute or two. Let stand at the corner of a hot plate for an hour and filter, or, let stand at room temperature for 12 hours and filter. Wash the residue of  $\text{BaSO}_4$  free of chloride. Ignite in a porcelain or platinum crucible over the Bunsen burner. Cool in a desiccator and weigh. From the weight of  $\text{BaSO}_4$ , calculate the % of  $\text{SO}_3$ .

NOTES:—

(1) As platinum crucibles are attacked by alkalis, the fusion should be carried out in an iron crucible. The addition of peroxide to sodium carbonate has for its object the oxidation of any sulphide that may have been inadvertently introduced or formed during the process of manufacture.

(2) The formation of the precipitate of barium sulphate in a coarsely granular condition is effected by adding the hot barium chloride solution to the boiling

hot solution of the sulphate. If the conditions specified are not closely followed, the size of the particles of the precipitate will be such that they will pass through the filter paper.

(3) Barium sulphate should not be ignited over a blast lamp, as it decomposes at the temperature of the blast lamp.

(4) As the reagents used are likely to contain sulphur in amounts which cannot be ignored, it is necessary to make, alongside of an assay a '*Blank run*' for their sulphur content. To do this, proceed as follows :—

Fuse in an iron crucible an equal weight of the mixture of  $\text{Na}_2\text{O}_2$  and  $\text{Na}_2\text{CO}_3$  formed by mixing the two in the same proportion as in the sample run. Extract the fusion with water and proceed exactly as in the sample run, taking care to keep the volume of water, acid and other reagents the same as in the assay. The weight of  $\text{BaSO}_4$  obtained by the blank run is deducted from the weight of  $\text{BaSO}_4$  obtained for the sample and calculation of the percentage of  $\text{SO}_3$  in the same is then made. The blank run becomes necessary also on account of the fact that the gas used for heating almost always contains sulphur as  $\text{H}_2\text{S}$ , which is burnt to  $\text{SO}_2$  and  $\text{SO}_3$  and absorbed during the fusion and subsequent operations. The chances of contamination from such a source are greater in Laboratories using coal-gas than in those like ours using oil-gas.

(5) Porcelain crucibles should not be used for fusions with  $\text{Na}_2\text{O}_2$ ,  $\text{Na}_2\text{CO}_3$ , etc.. The glaze is attacked and the crucible then becomes unserviceable for the ignition of precipitates, the smoothness of surface having been destroyed. Nickel crucibles may be substituted for effecting the fusion.



(6) Sodium peroxide should be removed from the container with a nickel spatula and transferred at once to the iron or nickel crucible in which the fusion is to be conducted. If transferred with a horn or celluloid spatula, these should be immediately washed with water; otherwise they are attacked by the peroxide which absorbs moisture from the air. If allowed to stand in the open air on paper containers, the peroxide causes the paper to inflame.

## CHAPTER IV

### Analysis of Pig Iron, Plain Carbon Steel and Alloy Steels.

#### EXPERIMENT 13.

#### Determination of Silicon in Pig Iron.

**Principle** :—Silicon which exists in Pig Iron as  $\text{FeSi}$  is oxidized by nitric acid to silicic acid, which is then dehydrated by evaporation to dryness with dil.  $\text{H}_2\text{SO}_4$ . The dried mass is dissolved in dil.  $\text{HCl}$  and the silica filtered off, dried, ignited and weighed. The percentage of silicon is then calculated from the weight of silica.

#### Solutions required :—

(1) Dilute Nitric Acid of S. G. 1.2. Pour 385 ml. of conc.  $\text{HNO}_3$  into a glass stoppered bottle containing 615 ml. water. Shake well.

(2) Dilute Sulphuric Acid of S. G. 1.18. Pour 167 ml. or 1 volume of conc.  $\text{H}_2\text{SO}_4$  into 833 ml. or 5 volumes of water contained in a beaker. When cold, transfer to a bottle. The concentrated acid should be poured into the water and not vice versa. The heat generated at the surface of contact of the two liquids by the latter method is so great that accidents are caused by the violent evolution and spirting of steam and liquid. Dilution of the conc sulphuric acid should not be carried out in thick-walled glass vessels such as reagent bottles, Winchester quart bottles, as such a procedure will lead to their cracking and breaking.

(3) Dilute Hydrochloric Acid of S. G. 1.1. Pour 465 ml. of the concentrated acid into a bottle containing 533 ml. of water.

**Procedure :—**Weigh a 0.500 gm. sample into a porcelain basin or a casserole of 200 ml. capacity, add 20 ml. dil.  $\text{HNO}_3$ , heat on the hot plate until a reddish brown ring forms on the basin near the edge of the liquid ; then add 10 ml. dil.  $\text{H}_2\text{SO}_4$ , cover with a cover-glass and evaporate to dryness in the fume chamber. The evolution of copious fumes of  $\text{SO}_3$  indicates dryness. Cool. Add 10 ml. of dil.  $\text{HCl}$ . Boil, dilute with water to about 40 ml. and filter. Collect the filtrate in a 250 ml. conical flask. Remove with a 'policeman' any residue adhering to the dish and transfer to the filter. Wash the dish and the filter paper with water and dil.  $\text{HCl}$  alternately until the edge of the paper shows no yellow colour. Drop the acid from a dropping bottle. Transfer the paper with the residue to a silica crucible, dry on the hot plate, ignite in a muffle, cool and weigh. From the weight of the silica obtained and the quantity of sample taken, calculate the percentage of silicon. Reserve the filtrate for phosphorus determination. (Expt. 14.)

**NOTES :—**

(1) Unless the pigs are machine cast, they are likely to be contaminated with sand particles mechanically taken up when they are cast in sand beds. Before weighing out for analysis, it is best to enclose a horse-shoe magnet in an ordinary paper envelope and pass it over a thinly spread layer of the drillings. By withdrawing the magnet from the envelope, the clean drillings fall off which are collected separately. A sample for analysis is weighed out from the clean drillings.

(2) Addition of larger quantities of the acids for dissolving is not harmful but the operation of drying is prolonged thereby.

(3) The ignition of the residue of  $\text{SiO}_2$  and graphite is best carried out in the muffle furnace and if the

muffle is red-hot, the time taken is only 10-15 minutes. Heating in a platinum crucible over a Bunsen burner even when carried out for 1 hour does not yield a perfectly white residue. The heat of a Teclu burner or of a blast lamp will yield a white residue if continued for an hour.

(4) The ignited residue should be perfectly white. A reddish colour indicates imperfect washing with dil. HCl.

#### EXPERIMENT 14.

##### **Determination of Phosphorus in Pig Iron.**

In technical practice, one and the same weighing serves for the determination of silicon and phosphorus. From the filtrate obtained by filtering off the  $\text{SiO}_2$ , phosphorus is determined.

**Solutions required:**—The same as in Experiment 16.

**Principle:**—See Experiment 16.

**Procedure:**—Evaporate the filtrate in the conical flask to near dryness, add 30 ml. of dil.  $\text{HNO}_3$  s.g. 1.20 and boil. When boiling, add a solution of  $\text{KMnO}_4$  until a pink colour is obtained which persists for about two or three minutes on boiling. Destroy the precipitate of  $\text{MnO}_2$  by adding a solution of  $\text{NaNO}_2$ . Boil to expel the oxides of nitrogen. Add 15 ml. conc.  $\text{HNO}_3$ . Cool to about  $70^\circ\text{C}$ . and add 50 ml. of ammonium molybdate solution. Shake vigorously for 5 minutes and filter. Wash the precipitate and flask first with dil.  $\text{HNO}_3$ , then with  $\text{KNO}_3$  solution until acid-free. Transfer the precipitate with the filter paper to the flask in which the precipitation was made and titrate with the standard solution of  $\text{NaOH}$ , using phenolphthalein as the indicator.

$$1 \text{ ml. NaOH} = 0.0002 \text{ gm P.}$$

## NOTES :—

(1) The precipitation of the pure phosphomolybdate takes place under the well defined conditions described in Experiment 16. The reasons for the modification, in the case of Pig Iron, of the procedure adopted for steel are given below :—

1. Evaporation of the filtrate to dryness brings about the expulsion of HCl, which would otherwise interfere with the formation of the yellow precipitate of ammonium phosphomolybdate.

2. Addition of nitric acid is necessary as the precipitation of phosphoric acid as phosphomolybdate is made always in a solution containing nitrates and free nitric acid. Other mineral acids exert a solvent action and interfere with the formation of optimum-sized particles of the precipitate suitable for filtration.

**Record and Calculation of Results:—**

Weight of Pig Iron = 0.5000 gm.

	NaOH	HNO <sub>3</sub>
Sample	15.0 ml.	7.0 ml.
Blank	15.0 ml.	15.0 ml.

As 1 ml. NaOH=0.0002 gm. P, the percentage of  
phosphorus =  $8 \times 0.0002 \times 200$   
=0.32

**EXPERIMENT 15.****Determination of Silicon in Plain Carbon Steel.  
Introductory:—**

In ordinary steels, the percentage of silicon is often about 0.03 and sometimes rises to about 0.2. The determination of silicon in tungsten and other alloy

steels is described along with the determination of the alloying elements.

### Principle :—

When the steel sample is treated with conc. HCl, evaporated to dryness, and baked, all the silicon is yielded as  $\text{SiO}_2$ . This is filtered off, after redissolving the dry mass in conc. HCl. The residue is ignited and weighed. From the weight of  $\text{SiO}_2$ , the silicon is calculated.

### Solutions required :—

1. Conc. HCl.
2. Dil. HCl S.G. 1.1. The same as in Expt. 13.

### Procedure :—

Weigh 5 gms. steel drillings into a 300 ml. casserole. Add 50 ml. conc. HCl. Cover with a cover glass and heat on a sand bath. When the vigorous effervescence is over, place on the wire gauze and heat directly over a Bunsen burner fitted with a mushroom top. Bake for half an hour after drying. Cool. Redissolve in 30 ml. conc. HCl by boiling for about 5 minutes. Add 30-40 ml. warm water. Filter. Wash residue and paper first with dil. HCl dropped from a dropping bottle and ultimately with warm water until free from chloride. Ignite in a silica, porcelain or platinum crucible over a Bunsen burner or a muffle furnace. Cool in a desiccator and weigh. From the weight of  $\text{SiO}_2$ , deduce that of silicon.

### NOTES:

(1) The difference between the methods adopted for the determination of silicon in the two materials, namely, Pig Iron and Steel, is due to the fundamental fact that whereas in the former it is present in amounts

varying from 0.8 to 3.8 %, in the latter it seldom exceeds 0.2%. Treatment with HCl will lead to the loss of some silicon as volatile compounds, such as silico-methane and silico-ethane, having respectively the formula  $\text{SiH}_4$  and  $\text{Si}_2\text{H}_6$ , in the former material, whereas in the latter such treatment has been shown by Arnold and others not to yield any  $\text{SiH}_4$ . A second reason for effecting the solution of the Pig Iron in nitric acid lies in the fact that the determination of phosphorus in that material goes with that of silicon. Treatment of the iron with HCl would lead to the loss of P as  $\text{PH}_3$ . Determination of phosphorus in steel does not go with that of silicon.

( 2 ) There is danger of the contents of the casserole boiling over if heated strongly, immediately after the addition of acid. Hence the necessity for gentle heating first, and stronger heating to dehydrate the silicic acid, afterwards. There is considerable tendency to spattering when nearing dryness. Regulation of heat prevents this.

( 3 ) The ignition of the residue in this case presents no difficulty, as there is no graphitic carbon to burn.

( 4 ) Purification of the silica by treatment with  $\text{H}_2\text{F}_2$  and  $\text{H}_2\text{SO}_4$  in the manner described in Experiment 56 is not necessary in the case of plain carbon steels.

#### EXPERIMENT 16.

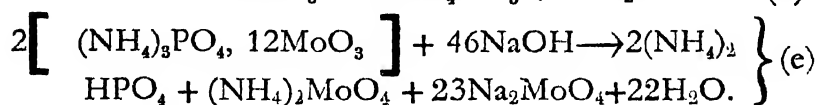
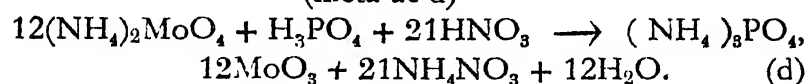
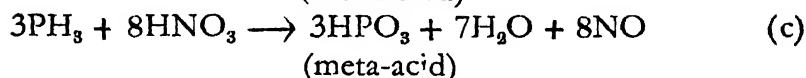
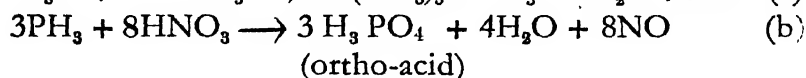
### Determination of Phosphorus in Plain Carbon Steel.

#### Principle :—

Phosphorus which exists in steel as phosphide of iron is oxidized by  $\text{HNO}_3$  to phosphoric acid. This acid exists partly in the meta and partly in the ortho

condition and is changed completely into the ortho condition by a solution of  $\text{KMnO}_4$ . The ortho acid of the formula  $\text{H}_3\text{PO}_4$  is then precipitated by  $(\text{NH}_4)_2\text{MoO}_4$  as  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$  (ammonium phosphomolybdate). The precipitate is filtered off, dissolved in a measured excess of standard sodium hydroxide and the excess titrated back with standard  $\text{HNO}_3$ , phenolphthalein being used as the indicator. From the amount of standard  $\text{NaOH}$  used, the percentage of phosphorus is calculated.

The following are the main reactions :—



### Solutions required for Phosphorus determination in Pig Iron and Steel.

1. Dil.  $\text{HNO}_3$ . The same as in Experiments. 13 and 15.
2.  **$\text{KMnO}_4$  solution.** Dissolve 25 gms. of the salt in 1 litre of distilled water.
3. **Potassium Nitrite Solution.** Dissolve 50 gms. of the salt in 1 litre of distilled water.
4. **Ammonia s.g. 0.95.** Add 750 ml. water to 250 ml. of ammonia of s.g. 0.88 contained in a litre bottle and mix by shaking.

5. **Ammonium Molybdate Solution (Johnson's Reagent).** Into a 1000 ml. beaker weigh 55 gms. of



ammonium molybdate and 50 gms. ammonium nitrate and add 40 ml. ammonium hydroxide (S.G. 0.95). Dilute to 700 ml. with water. Heat for about 30 minutes stirring once in a while until all the salts are in solution. Dilute to 1000 ml. with water. Let stand overnight. Filter through double-filter. Do not wash the residue. The solution thus obtained remains clear indefinitely, whereas that made differently throws down a deposit on standing, especially in hot countries like ours. The solution of ammonium molybdate is a 5.5% solution. 1 gm. of P yields about 60 gms. of the yellow phosphomolybdate precipitate. Ordinarily steels do not contain more than 0.05% P. 2 gms. sample will contain 0.001 gm. P. To precipitate this, 1.36 ml. of molybdate must suffice theoretically. But we generally add 40 to 50 times the volume theoretically necessary. The precipitation is complete only when such a large excess is present.

6. Nitric acid wash :—Dilute 32 ml. of acid of s.g. 1.20 to 1 litre with distilled water.

7. Potassium Nitrate wash :—Dissolve 1 gm. of the salt in 1 litre of distilled water.

8. Phenolphthalein indicator :—Dissolve 0.1 gm, in 100 ml. of ethyl alcohol or methyl alcohol.

9. **Standard Sodium Hydroxide Solution** :—Dissolve 6.5 gms, of purified NaOH in 100 ml. distilled water, add about 5 ml. of 1 %  $\text{Ba}(\text{OH})_2$  solution. Let stand 24 hours. Decant the liquid. Standardize it against pure oxalic acid or steel of known phosphorus content. Protect solution from carbon dioxide by soda lime tube. See Fig. 4. Soda-lime is made as follows :—Lime is slaked with a 10% solution of caustic soda. The lime thus slaked is heated over a Bunsen burner in

a silver or nickel dish until the mass clots up. This is then withdrawn, cooled, broken, up and sieved. 14-20 mesh grains are used.

10. Standard  $\text{HNO}_3$  :—Mix 10 ml. of  $\text{HNO}_3$  s.g. 1.42 and 1000 ml. distilled water in a bottle. Titrate the solution against standardized  $\text{NaOH}$  using phenolphthalein as indicator and make it equivalent to the  $\text{NaOH}$  solution by adding distilled water.

**Example** :—Suppose 20 ml. of  $\text{NaOH}$  solution requires 18 ml. To make  $\text{HNO}_3$  equal in strength to  $\text{NaOH}$ , 2 ml. water for every 18 ml. of the acid must be added.

**Procedure** :—Weigh into a 250 ml. Erlenmeyer flask a 2 gm sample of steel. Add *gradually* 30 ml. of 1.20 s.g.  $\text{HNO}_3$ . Bring into solution by gentle boiling. Add a few ml. of  $\text{KMnO}_4$  solution until a pink colour persists on boiling for 3 minutes. Destroy the precipitated  $\text{MnO}_2$  by adding a solution of potassium nitrite drop by drop. Continue boiling a minute or two after the  $\text{MnO}_2$  has been dissolved. Add 15 ml. conc.  $\text{HNO}_3$ . Cool to  $70^\circ\text{C}$ . Add 50 ml. of the ammonium molybdate solution. Shake vigorously for 3 minutes. Allow to stand for 5 minutes. Filter. Wash the flask and the filter paper containing the precipitate a few times with very dilute  $\text{HNO}_3$  and then with  $\text{KNO}_3$  solution until the filtrate is free from acid. Test as follows : Collect 5 ml. filtrate in a test tube, add one drop of phenolphthalein and one drop of the standard  $\text{NaOH}$  solution. If there is a pink colour, the precipitate is free from acid. Drop the filter paper with the precipitate into the flask in which the precipitation was made. Add from a burette from 10-15 ml. of the standard sodium hydroxide solution to the precipitate

in the flask. Shake well until the filter-paper is well macerated and there is no yellow tinge or stain on the macerated paper. Add 3-4 drops of phenolphthalein and then run in the standard  $\text{HNO}_3$  from a burette until the pink colour is just discharged.

### Record of Results and Calculation :—

Weight of steel taken 2 gms.

	NaOH	$\text{HNO}_3$
Sample	15.0 ml.	10.0 ml.
Blank	15.0 ml	15.0 ml.

1 ml. of NaOH = 0.0002 gm. of P.

The percentage of P in the steel is ( 15-10 or )  $5 \times 0.0002 \times \frac{100}{2}$  i.e. 0.05. From the equation (e) given above

it follows that 23 gm. molecules of NaOH correspond to 1 gm. atom of phosphorus. In Steel Works' laboratories it is found convenient to make the solution of NaOH of such a strength that 1 ml. of it will correspond to 0.0002 gm. P. 1 litre of this NaOH solution will be equal to 0.2 gm. P.

31 gms. of P will correspond to  $23 \times 40$  gms. NaOH

0.2 gm. of P „ „  $\frac{23 \times 40 \times 0.2}{31}$  gms. NaOH  
i. e. 5.934 gms.

5.934 gms. NaOH in 1 litre yields therefore the necessary standard solution. But as even purified sodium hydroxide may contain carbonate, the usual practice in preparing a standard solution of NaOH is as follows:—

About 6-7 gms. of NaOH are dissolved in water, the carbonate removed as  $\text{BaCO}_3$  by treatment with  $\text{Ba}(\text{OH})_2$  solution and the strength adjusted by dilution with carbonic-acid-free water, a steel of known phosphorus content being used in the adjustment of the strength of the solution.

## NOTES :—

(1) The precipitation of phosphorus as ammonium phosphomolybdate in a solution containing organic matter is not complete. The solution of steel in  $\text{HNO}_3$  contains organic (carbonaceous) matter which is destroyed by boiling with  $\text{KMnO}_4$  solution. Boiling with  $\text{KMnO}_4$  solution also effects the complete conversion of the meta phosphoric acid into the ortho acid, which alone is completely precipitated by means of  $(\text{NH}_4)_2\text{MoO}_4$  as the yellow phosphomolybdate.

(2) The precipitated  $\text{MnO}_2$  is brought into solution by treatment with  $\text{KNO}_3$ . Alternatively,  $\text{Na}_2\text{SO}_3$  or  $\text{FeSO}_4$  (phosphorus free) may be used.

(3) The precipitation of the phosphomolybdate takes place rapidly when the temperature of the solution in which P exists as  $\text{H}_3\text{PO}_4$  is kept at  $70^\circ\text{C}$ . prior to adding  $(\text{NH}_4)_2\text{MoO}_4$ . Vigorous shaking helps the formation and settling down of the precipitate.

(4) The addition of  $\text{NH}_4\text{NO}_3$  solution also hastens the formation of the precipitate.

(5) Nitric acid wash serves to remove the iron in a few washings.

(6) A solution of  $\text{KNO}_3$  in water is used as wash liquid, as this has no solvent action on the precipitate. Pure distilled water has a slight solvent action.

(7) The one important difference between the methods followed for P in steel and in pig iron lies in the fact that, whereas in the latter case the Si has to be removed as  $\text{SiO}_2$  by evaporation to dryness and filtration, in the former it is unnecessary to do so. The amount of Si in steel is very low, about .03-.08%. This though converted into  $\text{Si}(\text{OH})_4$  by  $\text{HNO}_3$  does not contaminate the precipitate of ammonium phosphomolybdate and

therefore does not yield a higher value for P than the true one. The amount of Si in pig iron, varying as it does from 1-4% yields  $\text{Si}(\text{OH})_4$  sufficient in amount to contaminate the phosphomolybdate precipitate. As the silicic acid would be titrated by NaOH, it is filtered off before proceeding further with P determination.

(8) Arsenic is present to some extent in steels made from pig irons containing it as an impurity. (Steels manufactured in India are free from it.) The element is changed to arsenic acid by the treatment with  $\text{HNO}_3$  above described. The arsenic acid so formed yields with ammonium molybdate a yellow precipitate but provided the conditions above described are closely followed, especially with regard to temperature at which the molybdate is added, and the interval before filtering off is not more than 5-10 minutes, no contamination arises from this source. But if it is to be removed before adding molybdate, the following is the procedure:—

Add to the nitric acid solution 50 ml. conc. HCl, evaporate to low bulk (15-20 ml.), repeat with 20 ml. more of conc. HCl. Add 30 ml. conc. HCl and 2-3 gms. pure zinc (free from arsenic). Most of the arsenic is expelled as  $\text{AsH}_3$  and the small amount still remaining is expelled by the addition of 10-15 ml. of HBr and taking down to low bulk,—about 40 ml. Arsenic tribromide is formed but, as this is volatile, it is expelled by boiling. The precipitation with molybdate is then proceeded with

### **Phosphorus in Steels containing Tungstèn and Vanadium. Introductory :—**

When the sample of steel is opened out with a mixture of HCl and  $\text{HNO}_3$  the elements W and V are oxidized to  $\text{WO}_3$  and  $\text{H}_2\text{VO}_4$ . The first is an insoluble

yellow residue, holding some P as phosphate. The second is in solution and gives rise to a precipitate, analogous in composition to the phosphomolybdate precipitate, on the addition of ammonium molybdate. Like the phosphomolybdate precipitate it is soluble in sodium hydroxide solution; hence the percentage of phosphorus obtained by the alkalimetric titration incorrect. By the modification described below, correct determination of phosphorus is made on steels containing W and V.

**Solutions required:**—The same as in Experiment 17.

**Principle:**— •

When the steel sample is dissolved in a mixture of conc.  $\text{HNO}_3$  and conc.  $\text{HCl}$ , evaporated to dryness and baked, the elements tungsten and vanadium form the yellow and the brick-red oxide respectively. On redissolving the baked residue in 1:1  $\text{HCl}$  and filtering, a large part of the phosphorus goes into the filtrate and a small part remains with the residue of  $\text{WO}_3$  on the filter paper, the vanadium passing into the filtrate as  $\text{VCl}_5$  or as  $\text{VOCl}_2$ .

The removal of the small amount of P from the  $\text{WO}_3$  residue is effected as follows :—Solution of the residue in ammonia, treatment of the solution to slight acidity with  $\text{HCl}$ , addition of a gram of alum, followed by treatment with ammonia to slight alkalinity, filtration, resolution of the residue on the filter paper in dil.  $\text{HCl}$  and its addition to the main filtrate. The treatment at this stage consists in the repeated evaporation (twice will do.) with conc.  $\text{HNO}_3$  to get rid of  $\text{HCl}$ . From this point, the procedure is exactly identical with the one for the determination of phosphorus in plain carbon steels. The interference from vanadium is prevented by the addition of a large volume of conc.  $\text{HNO}_3$  (40 ml.) before the addition of the molybdate reagent. It must be

remembered that this reagent, unlike the one in common use, is a faintly ammoniacal water solution of ammonium molybdate, and it gives, according to C. M. Johnson, correct results for P in steels which may contain even as high a percentage of vanadium as 2.6.

The principle of separation of tungstic acid from phosphoric acid by the addition of alum is as follows :—

Ammonia dissolves  $\text{WO}_3$  and  $\text{H}_3\text{PO}_4$  forming  $(\text{NH}_4)_2\text{WO}_4$  and  $(\text{NH}_4)_3\text{PO}_4$  respectively. When the solution obtained is made slightly acid with  $\text{HCl}$ ,  $\text{H}_3\text{PO}_4$  is formed with the separation of  $\text{WO}_3$ . On the addition of alum followed by ammonia to slight alkalinity a precipitate of  $\text{AlPO}_4$  forms with a small amount of  $\text{Al}(\text{OH})_3$ ,  $\text{WO}_3$  remaining in solution as  $(\text{NH}_4)_2\text{WO}_4$ . The precipitate is filtered off, washed free of  $(\text{NH}_4)_2\text{WO}_4$ , then dissolved in  $\text{HCl}$  and the solution mixed with the main filtrate.

### Procedure :—

Dissolve 1 gm. of the steel drillings in a porcelain dish (4" size) in a mixture of 50 ml. conc.  $\text{HNO}_3$  and 30 ml. conc.  $\text{HCl}$ . Evaporate to dryness on a sand-bath with cover-glass on. Bake at 300 to 500°C., after removing cover-glass, to destroy organic matter. Cool. Redissolve in 30 ml. conc.  $\text{HCl}$  with the aid of heat. Dilute with water to about 100 ml. Filter using paper pulp and filter-pump. Wash 5 times with dil.  $\text{HCl}$  and hot water. Evaporate the filtrate to a low volume. Meanwhile dissolve the precipitate on the paper with hot dil.  $\text{NH}_4\text{OH}$  (10 ml. of Bench Reagent are diluted to 40 ml.). Pour back and forth to dissolve completely. Wash first with hot dilute ammonium hydroxide twice and then with hot dilute  $\text{HCl}$  (1 : 10) three or four times. To the filtrate made faintly acid with  $\text{HCl}$ , add 1 gm. of powdered potassium aluminium sulphate or aluminium sulphate

and then ammonium hydroxide in slight excess. Use litmus paper to indicate alkalinity. Boil for three minutes; filter, wash the paper with hot water containing a little ammonium chloride, three or four times. Reject the filtrate. Dissolve the precipitate, which is now free from tungstic acid but which contains all the P, originally associated with the tungstic acid, as  $\text{AlPO}_4$ , in hot dilute HCl. Pour the acid through several times to dissolve the precipitate completely. Add this liquid to the main filtrate. Concentrate to low bulk after the addition of 40 ml. conc.  $\text{HNO}_3$ . Repeat concentrating after the addition of 20 ml. more of conc.  $\text{HNO}_3$ . At this stage, proceed, as in plain carbon steels, with the addition of ammonium molybdate, filtration and titration.

NOTES :—

(1) As described in the main process for the determination of P in plain carbon steels, the solution from which P is to be thrown down as  $(\text{NH}_4)_3\text{PO}_4$ , 12  $\text{MoO}_3$  must, as far as possible, be free from chlorides and HCl. With this object, the evaporation of the combined filtrates to low bulk repeatedly with conc.  $\text{HNO}_3$  is adopted.

(2) The interference caused by vanadium may also be eliminated by the careful addition of  $N/10$   $\text{FeSO}_4$  to the solution ready for precipitation after the removal of  $\text{WO}_3$ , until the yellow colour due to vanadic acid is destroyed. In this case the addition of 40 ml. conc.  $\text{HNO}_3$  before adding  $(\text{NH}_4)_2\text{MoO}_4$  is not necessary; about 10 ml. of it is enough. The hitting of the point at which the vanadic acid is completely reduced is rather difficult without the use of indicators; a drop of the liquid is tested with  $\text{K}_3\text{Fe}(\text{CN})_6$  solution placed on a porcelain tile. A blue colour just appearing shows that the addition of  $\text{FeSO}_4$  is enough. In case the vanadium determination has been made on a separate



sample, the required number of ml. of  $N/10$   $\text{FeSO}_4$  is added and the determination of P then proceeded with as usual. The reaction that takes place on the addition of  $\text{FeSO}_4$  consists in the reduction of vanadic acid to vanadyl sulphate  $\text{V}_2\text{O}_5(\text{SO}_4)_2$  which, unlike  $\text{H}_3\text{VO}_4$ , does not form a precipitate with  $(\text{NH}_4)_2\text{MoO}_4$ . In case the precipitation is made without reduction of vanadic acid, the precipitate of  $(\text{NH}_4)_2\text{PO}_4 \cdot 12\text{MoO}_3$  is rather slow in forming and settling and a period of 12 hours may be necessary for the complete settling down of the same.

### EXPERIMENT 18.

#### Determination of Sulphur in Pig Iron and Steel. Principle :—

Sulphur which exists in Pig Iron and Steel as either  $\text{MnS}$  or  $\text{FeS}$  is oxidized by means of aqua regia to  $\text{H}_2\text{SO}_4$ . This is fixed as  $\text{Na}_2\text{SO}_4$  by adding solid  $\text{Na}_2\text{CO}_3$ . The silica that separates on evaporating the solution is filtered off after dissolving the soluble salts again.  $\text{Na}_2\text{SO}_4$  in the filtrate is precipitated as  $\text{BaSO}_4$  by means of  $\text{BaCl}_2$ . The precipitate is filtered off, ignited and weighed. From the weight of  $\text{BaSO}_4$ , the percentage of sulphur is calculated.

#### Solutions required :—

- (1) Pour 350 ml. of water into a bottle containing 650 ml. of ammonia of s.g. 0.88. Mix by shaking.
- (2) Dissolve 2.5 gms. of  $\text{BaCl}_2$  crystals in 100 ml. water.

**Procedure** :— Weigh 5 gms. of the sample into a 400 ml. beaker. Add a mixture of 40 ml. conc.  $\text{HNO}_3$  and 5 ml. conc.  $\text{HCl}$ . ( $\text{HCl}$  must not be added alone at first). Heat on the hot plate or over a burner in the fume chamber. When about 5 ml. of the liquid remain in the beaker, transfer to a porcelain dish or casserole.

Rinse the beaker with a few ml. of water, add a pinch of pure  $\text{Na}_2\text{CO}_3$  and evaporate to dryness, constantly stirring with a glass rod. Ignite at a dull red heat to destroy organic matter and to dehydrate  $\text{Si}(\text{OH})_4$ . Cool. Dissolve in 25 ml. conc.  $\text{HCl}$ . Dilute with water to about 50 ml. and filter off  $\text{SiO}_2$ . Wash with 1:10  $\text{HCl}$ . To the filtrate which should be about 350-400 ml., add an excess of ammonia (solution 1). Keep the liquid at  $70^\circ\text{C}$ . for about 15 minutes. Pour into a 500 ml. measuring flask. Cool. Make up to the mark. Mix well. Pour through a large dry filter, and collect the filtrate in a clean, dry beaker. Pipette off 250 ml. into a beaker. Add 2 or 3 drops of methyl orange to the 250 ml. portion which has been pipetted off. Neutralize with  $\text{HCl}$  and then add 1 ml. conc.  $\text{HCl}$  in excess. Heat the solution to boiling, add 100 ml. of Solution No. 2 which has been heated to boiling and stir vigorously. Allow to stand in a warm place for half an hour.

Filter, washing the precipitate three times by decantation with boiling water, then transfer the same to the filter, wash until free from chlorides, dry somewhat and ignite in a porcelain or platinum crucible over an ordinary Bunsen burner (do not use the blast lamp). Cool in a desiccator and weigh. From the weight of  $\text{BaSO}_4$  calculate the percentage of S in the sample of Pig Iron or Steel.

Run a 'Blank' for the sulphur in the reagents used, alongside of the assay. Use the same amounts of reagents, water, etc.

Weight of sample of pig iron = 5 gms.

Weight of  $\text{BaSO}_4$  brushed off to the scoop = 0.0178 gm.

( sample )

" " " " " " " = 0.0030 gm.

( blank )

$$\begin{aligned}\text{Hence \% S in the sample} &= 0.0148 \times 0.1373 \times 40 \\ &= 0.066\end{aligned}$$

NOTES:—

(1) As evaporation to dryness and ignition of the contents cannot be carried out in a glass-beaker without cracking it, these are done in a porcelain basin or casserole, the liquid, when of a low bulk, having been transferred to it from the beaker.  $\text{Fe}_2(\text{SO}_4)_3$  formed by the oxidation of  $\text{FeS}$  by aqua regia is decomposed at temperatures much above  $100^\circ\text{C}$ . As ignition of the dried contents is necessary to dehydrate  $\text{H}_4\text{SiO}_4$  and to destroy organic matter, it becomes imperative to fix the sulphuric acid in a form not volatilised at the temperature at which the ignition of the contents is conducted. With this object, a pinch of pure  $\text{Na}_2\text{CO}_3$  is added. The sulphuric acid is thereby fixed as  $\text{Na}_2\text{SO}_4$ . This does not decompose at the temperature necessary for dehydrating  $\text{H}_4\text{SiO}_4$  and for destroying organic matter.

(2) The precipitate of  $\text{BaSO}_4$  when formed in a solution containing a large amount of  $\text{FeCl}_3$  has a tendency to adsorb it. Therefore all the iron is removed as  $\text{Fe}(\text{OH})_3$  by treating with  $\text{NH}_4\text{OH}$ .

(3) The method here adopted is what is known as fractional filtration.  $\text{Fe}(\text{OH})_3$  precipitate is very bulky and the sulphates associated with it can be removed only by repeated washings, an operation taking much time. Hence, only a portion of the 500 ml. is filtered off. 250 ml. of the solution used for the final precipitation of  $\text{H}_2\text{SO}_4$  as  $\text{BaSO}_4$  represent a fraction ('i. e. ) one-half of the original weight used for the analysis.

(4) Neutralization of the excess of ammonia is necessary.  $\text{HCl}$  in large quantities interferes with the formation of the precipitate and the size of its grains.

(5) Ignition over a blast lamp decomposes  $\text{BaSO}_4$  partially.

(6) When ignited over a Bunsen burner in a crucible partially kept open, reduction of the sulphate by the carbon of the filter-paper does not take place. Fig. 5 shows the manner of supporting the crucible. The heating of the ppte. is carried out from its surface inwards, the flame being deflected from the lid. Mechanical loss of particles of the ppte. is also prevented thereby.

The method detailed above is known as the 'Long Method'. This is used, without any modification, also for S in steel. In all cases of dispute regarding the accuracy of the "Evolution Method", described in the next experiment and followed as the routine method in Steel Works' Laboratories, the 'Long Method' is used. The same 'Long Method' is also used in the determination of sulphur in such materials as iron pyrites, chalcopyrites, lead sulphide, etc. This method is also known as the umpire or the referee method.

## EXPERIMENT 19.

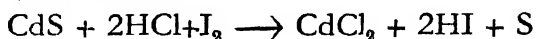
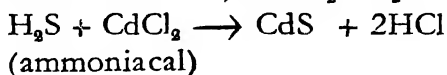
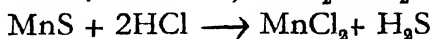
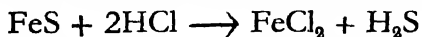
### Determination of Sulphur in Pig Iron and Steel. ( Evolution-Titration Method. )

#### Principle :—

Sulphur present in pig-iron and steel as  $\text{FeS}$  or  $\text{MnS}$  is evolved as  $\text{H}_2\text{S}$  on treating the sample with  $\text{HCl}$ . This gas is passed through a solution of ammoniacal cadmium chloride when yellow cadmium sulphide is precipitated. This is treated with a solution of iodine of known strength in excess in the presence of  $\text{HCl}$  and the excess of iodine titrated back with standard sodium thiosulphate solution. The amount of iodine

solution used is a measure of the sulphur content in the sample of pig-iron or steel.

The reactions involved are as follows :—



### Solutions required:—

1. Dilute HCl of s.g. 1.1.
2. Ammoniacal Cadmium Chloride :—Dissolve 4 gms. of cadmium chloride in 100 ml. water and add an equal volume of ammonia of s.g. 0.88. 5 ml. of this solution will precipitate 0.0145 gm. S as CdS. This volume of solution is sufficient for precipitating S in materials containing up to 0.29% S, when only 5 gms. of the material are used for an experiment.
3. **Starch solution:**— Make into a paste 0.5 gm. of ordinary wheat starch or 0.1 gm. soluble starch by mixing it with about 5 ml. water. Pour the paste into 100 ml. of boiling water. Continue boiling for 2 minutes. Cool. Keep in a corked bottle. The solution does not keep well. It is best to prepare it fresh once every two days.
4. Dissolve 4 gms. of pure potassium iodide in 100 ml. distilled water.
5. Dilute  $\text{H}_2\text{SO}_4$  of s.g. 1.18.

### Standard solutions :—

1. Iodine solution of approximately N/32 strength. Dissolve 6 gms. of potassium iodide free from iodate in about 10 ml. water in a 100 ml. conical flask. To the solution add about 4 gms. of iodine. Shake until

the iodine completely dissolves. Make the solution to 1 litre and stock in an amber-coloured bottle having a glass-stopper.

2. Approximately  $N/32$  Sodium Thiosulphate solution. Dissolve 7.75 gms. of the thiosulphate and 1.7 gms. of potassium carbonate in 1 litre of water. Keep in a litre bottle.

3.  $N/30$  Potassium Permanganate solution. Dilute 75 ml. of the permanganate solution used in the determination of iron in iron ore exactly to 250 ml. in a 250 ml. graduated flask.

Take about 20 ml. of the potassium iodide solution (No.4) in a 250 ml. conical beaker. Add about 5 ml. of the dilute sulphuric acid and about 20 ml. water. Introduce from a burette exactly 20 ml. of the diluted permanganate solution. Iodine is liberated. To titrate this, run from a second burette thiosulphate solution until the liquid in the beaker is pale yellow. Add 2 ml. of the starch solution at this stage and continue the addition of the thiosulphate until there is only a faint blue colour. Repeat two times more. Take the mean value of the volumes of the thiosulphate solution used.

75 ml.  $N/10$   $KMnO_4$  diluted to 250 ml. exactly.

Strength of the diluted  $KMnO_4$  solution is  $\frac{75}{250} \times \frac{N}{10}$   
or 0.03  $N$ .

0.03 $N$ $KMnO_4$		$Na_2S_2O_3$
1	20.0 ml.	18.0 ml.
2	20.0 ml.	18.0 ml.
3	20.0 ml.	18.0 ml.

The strength of the thiosulphate solution is  $\frac{20}{18} \times 0.03 \text{ N} = 0.0333 \text{ N}$ .

Fix the strength of the iodine solution by titrating it against thiosulphate solution. Proceed as follows:—

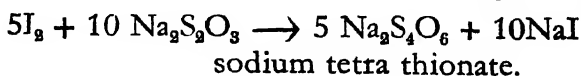
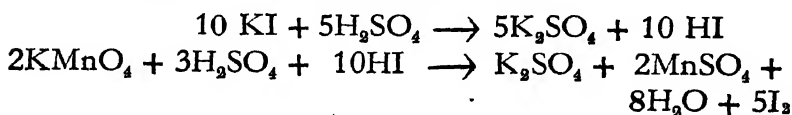
Run 20 ml. of the iodine solution from a burette with glass-cock into a 250 ml. beaker. Add the thiosulphate solution until the liquid in the beaker is light yellow. Introduce 2 ml. starch solution and finish by running the thiosulphate until the colour is only a light blue. Repeat twice.

Let the mean value of the thiosulphate solution be 18 ml. Then, the strength of the iodine solution is

$$\frac{18}{20} \times 0.0333 \text{ N} = 0.03 \text{ N}.$$

1 ml. of 0.03 N iodine solution = 0.00048 gm. S.

The reactions in standardizing the thiosulphate solution against  $\text{KMnO}_4$  are as follows:—

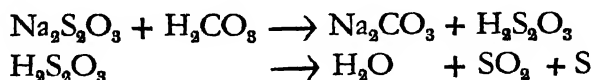


Notes on preparing the standard solutions of iodine and thiosulphate:—

1. As iodine is not readily available in a great state of purity, a standard solution of it cannot be made by dissolving an exactly weighed quantity of it in an exactly measured volume of water. Hence, the method of preparing a solution and then the fixing of its strength against standard sodium thiosulphate solution in the manner described has to be adopted. Iodine

is only slightly soluble in water but it is very soluble in a concentrated solution of potassium iodide.

2. The addition of  $K_2CO_3$  to the solution of thio-sulphate serves to react with the  $CO_2$  in solution in the distilled water, thereby forming the bicarbonate and preventing the following reactions :—



The sulphurdioxide thus formed will react with more iodine than the thiosulphate solution which is not so decomposed.

3. Determinations involving the use of standard iodine solution are known as '*Iodometric determinations.*'

**Procedure :—**

Fit up the apparatus as shown in Fig. 6a. Introduce

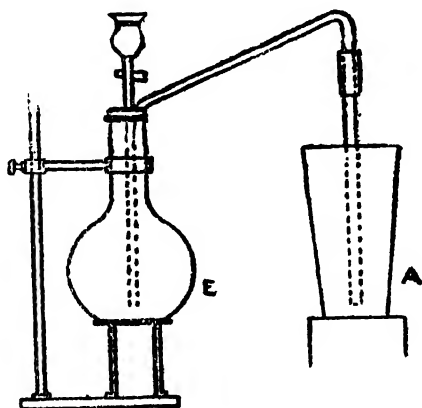


Fig. 6 a

5 gms. of the sample into E. Close with the cork. Place 5 ml. of the cadmium chloride solution in A, add



10-15 ml. strong ammonia and dilute to about 125 ml. with water. Run from the dropping funnel 50-75 ml. of HCl of 1.12 s.g. . Raise to a boil and keep gently boiling until all the metal goes into solution. When the speed of evolution of gas has considerably slackened, disconnect the delivery tube dipping into the absorption vessel, turn the Bench-gas off, pour the liquid with the precipitate into a 500 ml. beaker, rinse A twice with water, pour the rinsings into the beaker and place the delivery tube in the beaker. Add from a burette 10-15 ml. of the standard iodine solution, 30 ml. of HCl of s.g. 1.1 and titrate back the excess of iodine against standard sodium thiosulphate, using 2 ml. of starch solution as indicator towards the end. The thiosulphate is run until only a faint blue colour is left.

#### NOTES :—

(1) This method yields results checking fairly with those by the gravimetric method only when the evolution of gas is very rapid. The rapidity of evolution must be so great that some of the liquid in the absorption vessel is about to be ejected out. Slow evolution tends to the formation of a compound of C, H and S in the flask E. This compound is with difficulty volatile and even when volatilized from E is not absorbed by  $\text{CdCl}_2$  yielding  $\text{CdS}$ .

(2) Ammoniacal cadmium chloride is used as the ammonia reacts with the HCl, a product of double decomposition between  $\text{H}_2\text{S}$  and  $\text{CdCl}_2$ , thus preventing the solution of  $\text{CdS}$  precipitate. The reaction  $\text{CdCl}_2 + \text{H}_2\text{S} \rightleftharpoons \text{CdS} + 2\text{HCl}$  proceeds in one or the other direction according as ammonia or acid is in excess.

(3) The apparatus shown in Fig. 6 b includes a condenser. Any HCl distilled off with steam is condensed and returned to the evolution flask.

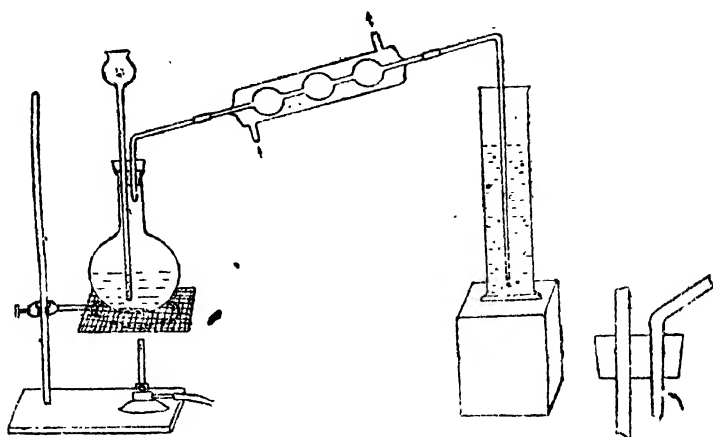


Fig. 6 b

condensed and returned to the evolution flask. It is more efficient than that shown in Fig. 6 a. The bent tube through which the evolved gases escape has a small hole at the side about 1cm. from the lower end. This helps the regular flow of gases. Condensed acid drops collecting at the end, will check the passage of gas.

(4) The hydrochloric acid used for evolution and titration must be free from chlorine and  $\text{FeCl}_3$  which impurities are commonly present in the acid. These oxidize the  $\text{H}_2\text{S}$  that is liberated and lead to low results.

(5) Though salts like  $\text{HgCl}_2$ ,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ ,  $\text{CuSO}_4$  will yield the respective sulphides with  $\text{H}_2\text{S}$ , they are not generally used because the sulphides of these metals are not soluble in HCl and therefore are not suitable for titration with iodine.

(6)  $\text{Dil. H}_2\text{SO}_4$  is very slow in its action on pig iron and  $\text{conc. H}_2\text{SO}_4$  has an oxidizing action on the  $\text{H}_2\text{S}$ . Therefore these cannot be employed for the liberation of  $\text{H}_2\text{S}$ .

(7) Provided the evolution is rapid by quick heating up, there is no need to pass a current of  $N_2$  or  $CO_2$  through the evolution flask to carry over any  $H_2S$  that may remain in the flask.

(8) The exact value per cubic centimetre of the iodine solution in terms of sulphur is fixed in Steel Works' Laboratories by putting a sample of steel of known sulphur content through the operations described for the sample under test. The following example will make the process of fixing the strength of iodine solution clear.

5 gms. steel of 0.065% S required :

Iodine

Thiosulphate

15.5 ml.

7.8 ml.

Relation of the strength of Iodine to that of the Thiosulphate was obtained by adding 20 ml of Iodine solution to the liquid left after the above titration and adding thiosulphate until the blue colour was just destroyed. This point was reached on the addition of 18 ml. of the thiosulphate solution.

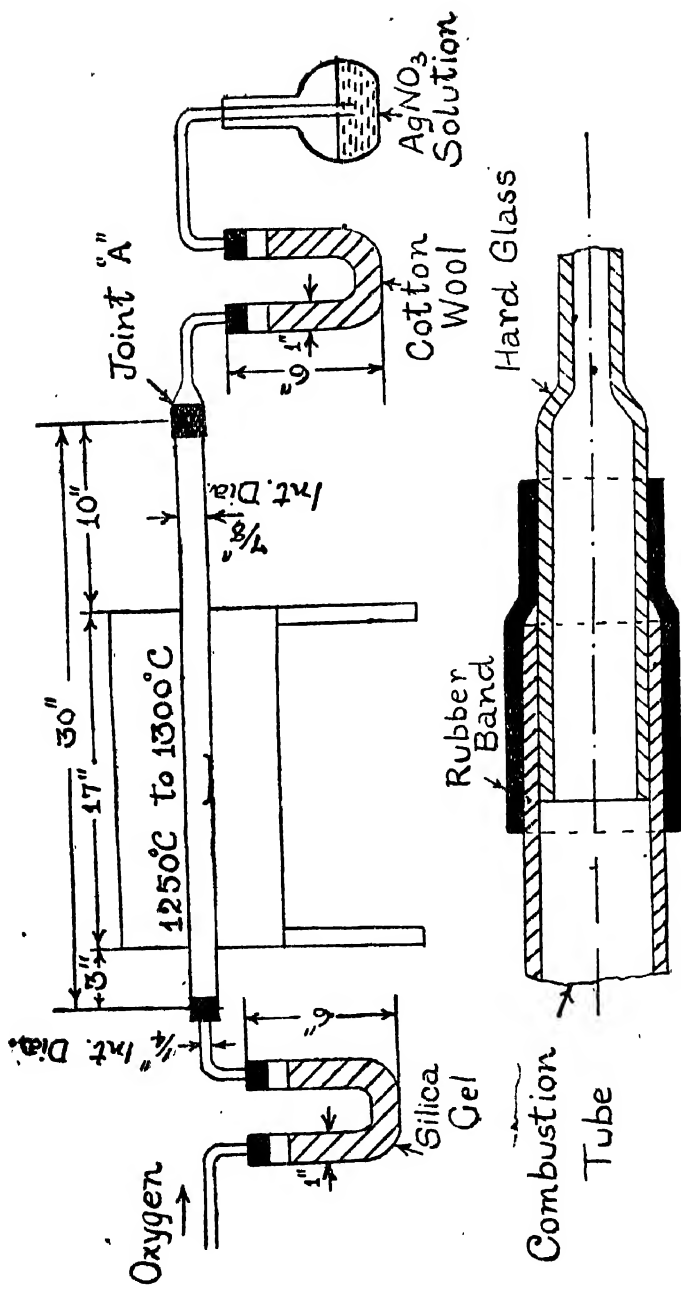
Hence, volume of iodine solution used up to react with  $H_2S$  is  $15.5 - \frac{7.8 \times 20}{18}$  i.e.  $15.5 - 8.7 = 6.8$  ml.

6.8 ml. of  $I_2$  corresponds to 0.065% S, on 5 gm. sample.

Hence, 1 ml. of  $I_2$  „ 0.0096% „ „

(9) Some alloy steels do not yield all their S by the above treatment. In such cases, an annealing treatment prior to running for S is necessary. This consists in heating 5 grams of the sample, wrapped in filter paper, in a porcelain crucible covered with lid, to  $750^\circ$  -  $850^\circ$  C. and cooling it slowly.





Detail of Joint "A"

Fig 7. To face p. 111.

## EXPERIMENT 20.

**Determination of Sulphur in pig Iron and Steel  
( The Combustion Method )****Principle :—**

When a current of oxygen is passed over a sample of the material contained in a boat and heated to a temperature of  $1250^{\circ}$  to  $1300^{\circ}\text{C.}$ , the sulphur is burnt quantitatively to sulphur dioxide which is passed through a solution of silver nitrate. Silver sulphite is formed and an equivalent amount of nitric acid is liberated. This is titrated against a standard solution of sodium hydroxide, methyl red being used as an indicator. From the volume of standard NaOH solution used, and the weight of drillings taken, the percentage of sulphur is calculated.

**Solutions required :—**

1. Silver Nitrate solution: 0.1 gm. of the pure substance is dissolved in 100 ml. distilled water.

2. Standard NaOH solution. 0.12 gm. of the caustic soda purified by alcohol is dissolved in 100 ml of distilled water. The strength of the solution in terms of normality is fixed by titrating against pure oxalic acid solution.

3. Methyl Red. Dissolve 0.05 gm. of methyl red in 800 ml. of ethyl alcohol and dilute to 1 litre with distilled water. Use about 10 drops of the indicator for each titration.

**Procedure :—**

Fit up the apparatus as shown in Fig. 7.

F is an electrically heated furnace capable of giving temperatures of the order of  $1300^{\circ}\text{C.}$  The attainment of such a high temperature is made possible by the use

of 'silit' or 'carborundum' heating elements. The combustion tube is preferably made of fused alumina, although an unglazed porcelain tube will serve and is about 30" long and 7/8" diameter with rubber corks at each end, having one hole each. At the inlet end I, the prolong  $P_1$  ( 6"  $\times$  7/8" ) is filled two thirds with soda-asbestos and the remaining one-third with anhydrous calcium chloride. Beyond this, there is a small layer of glass wool. At the forward end E, there is a U tube each limb of which is 6" long and 1/4" in diameter. This is immersed in cold water contained in a beaker.

The second prolong  $P_2$  with the bent end (6"  $\times$  7/8") is filled loosely with cotton wool. The bent portion dips into the solution of silver nitrate contained in a large size test tube or jar J of about 100. ml. capacity.

Weigh out 1 gm. of the material into a porcelain or alundum boat 3" long, 1/2" wide and 3/8" deep. Spread the same evenly over the entire length of the boat. Introduce the boat into the hottest part of the furnace. Pass a current of oxygen at a rapid rate (about 2000 ml. in one minute ) over the heated sample. The combustion will be over in 1-2 minutes. Withdraw J. Stop the supply of oxygen. Withdraw the boat. Titrate the solution in J against sodium hydroxide solution using methyl red as indicator.

Put a steel sample weighing 1 gm. and of known sulphur content through the process exactly as before. The number of ml. of sodium hydroxide used gives the data for calculating the sulphur content.

### Example :

1 gm. standard steel sample of 0.05% S consumed 8.0 ml. of NaOH solution.

1 gm. sample of unknown steel consumed 10.0 ml.  
Hence S in unknown sample is  $.05 \times 10 + 8 = 0.063\%$

NOTES :—

(1) As in the experiment on carbon determination by the combustion method, a current of oxygen should be drawn from a Pepys gas-holder. For filling it with oxygen from a cylinder of the compressed gas, see Expt. 24.

(2) Iron oxide, formed during the combustion, is spattered on to the wall of the combustion tube, is scraped out with a stout steel wire and blown off after each combustion. If this is not done, the introduction of the boat with the sample becomes difficult. Also, the combustion tube will crack with the accumulation of the spattered oxide.

(3) One inch length of the cotton wool filling the prolong  $P_2$  must be changed after each experiment. The whole of the cotton wool must be changed after about 12 determinations have been made.

(4) Soda-asbestos is prepared by soaking asbestos fibre, suitable for use in the Gooch crucible, in a normal solution of sodium hydroxide, drying it and heating to a temperature of about  $400^\circ\text{C}$ . This is for purifying oxygen. Silica gel has been substituted for soda-asbestos by a committee investigating this method.

(5) An alternative method of determination of sulphur is based on the combustion of sulphur to sulphur dioxide at about  $900^\circ\text{--}1000^\circ\text{C}$ ., oxidation of the sulphur dioxide to sulphur trioxide by passage through a measured volume of a standard solution of sodium hydroxide containing hydrogen peroxide and titrating the amount of unused sodium hydroxide, using methyl orange as indicator. The drawback of the method lies in



that the sulphur is not quantitatively burnt to sulphur dioxide at  $900^{\circ}$ – $1000^{\circ}\text{C}$ .

(6) Yet another method of determination is based on the oxidation of the sulphur dioxide formed by combustion at temperatures of the order of  $900^{\circ}$ – $1000^{\circ}\text{C}$ . by a standard solution of iodine, through which it is passed. The objection to this method is that the sulphur is not quantitatively burnt to sulphur dioxide.

(7) To increase the efficiency of absorption of the sulphur dioxide formed, in the solution of silver nitrate, the use of sintered Jena glass disc, porosity G1, has been very strongly recommended by committees investigating the combustion method. The sketch of the absorption vessel is given in Fig. 8

(8) The joint between the combustion tube and the glass-tubing is effected by grinding the two so as to be gas-tight. Such joint eliminates the use of rubber and the consequent absorption of the oxides of sulphur by it.

(9) The combustion method for sulphur determination with the absorption of sulphur dioxide in a solution of silver nitrate was developed in Sweden and is described in *Jernkontorets Annaler*, 1938, vol. 122, No. 1, pp. 49-51.

## EXPERIMENT 21.

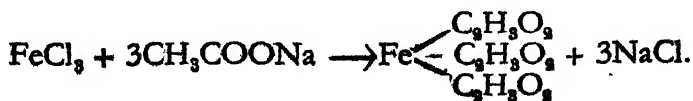
### **Determination of Manganese in Pig Iron and Steel. ( Gravimetric Method. )**

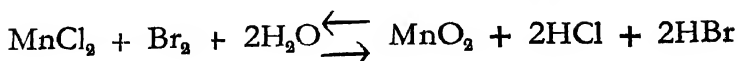
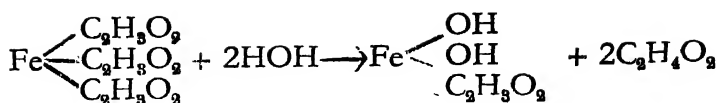
Manganese is present in plain carbon steels and pig irons in amounts varying from 0.4 to 1.0%. It is present in alloys like spiegel and ferro-manganese, from 10 to 30% in the former, and from 40 to 80% in the latter. In crushing machinery parts it is present to the extent

of 14%. The forms in which it occurs in iron and steel are  $\text{MnS}$  and  $\text{Mn}_3\text{C}$ . The gravimetric method described is the one to which an appeal is made when there is a discrepancy between the results obtained by two analysts working on the same material and using the same volumetric method.

The methods adopted vary according as the amount present is small or large. The usual plan of adopting the same method for large percentages as for small ones by starting with a proportionately smaller quantity of the material is not an ideal one, in-as-much as accuracy is sacrificed to rapidity of analysis. The standard procedures adopted in the determination of small and high percentages are described in this and the following experiments.

**Principle :—**When manganese chloride solution free from iron is treated with bromine water and sodium acetate or ammonia, hydrated oxide of manganese of the formula  $\text{MnO}(\text{OH})_2$  is precipitated. This is filtered off, ignited and weighed as  $\text{Mn}_2\text{O}_3$ . To secure a solution of manganese chloride free from iron, the well-known separation of iron as basic ferric acetate is adopted. The principle of the separation consists in the fact that when, to a solution of ferric and manganese chlorides, only very slightly acid and very dilute, a solution of sodium acetate is added and the mixture raised just to the boiling point, all the iron is thrown down as a reddish brown precipitate of basic ferric acetate, the manganese remains in solution and is obtained by filtration. The reactions that take place are as follows:—





To carry the reaction indicated by the lower arrow in the last equation to completion, it is necessary that the medium should contain either excess of sodium acetate or ammonia.

### Solutions required :—

(1) Sodium carbonate solution:—6 gms. in 100 ml. water.

(2) Sodium acetate solution :— a saturated solution of it made at room temperature.

(3) Dilute ammonia of 0.96 s.g. . Pour 7.50 ml. water into 250 ml. of ammonia in a litre bottle.

### Procedure :—

**Step 1 :—**Dissolve 1 gram sample of steel in 15 ml. of conc. HCl in a 200 ml. beaker covered with a cover glass. When the steel has gone into solution add 1-2 ml. of conc. nitric acid to oxidize the ferrous iron to the ferric condition. Boil until the nitrous fumes are expelled. Transfer the solution to a 1000 ml. beaker. Rinse the small beaker three or four times and transfer the rinsings to the litre beaker. Dilute the solution to about 300 ml. . Add, in small quantities at a time and with vigorous stirring, the solution of sodium carbonate until the precipitate of ferric hydroxide that is formed is no more dissolved. There should be only a very small quantity of precipitate floating. At this stage, the contents of the beaker are dark red in colour when seen by reflected light. Dilute to a volume of 800 ml.

with water, heat, and, when about to boil, add 1 ml. of a saturated solution of sodium acetate. Boil for a minute after the addition of sodium acetate solution. Transfer to a litre measuring flask and make up to the mark with boiling water. Mix by pouring back and forth into a clean dry one litre capacity beaker. Filter through a dry fluted filter paper into a 500 ml. measuring flask. Place the 500 ml. flask in a boiling water bath and pipette off sufficient of the filtrate so that only enough remains in the flask to reach to the mark at the temperature of the bath.

**Step 2 :—**Precipitation of the manganese as  $\text{MnO}(\text{OH})_2$  by means of bromine and ammonia : Cool the solution in the measuring flask to room temperature, transfer it to a 600 ml. beaker, rinse the 500 ml. flask two times and add the rinsings to the beaker. Add 1-2 ml. of liquid bromine (care) and stir with a glass rod. There must be a few drops of bromine left at the bottom of the beaker. Add ammonia until the liquid smells of it. About 25-30 ml. of ammonia of s.g. 0.96 will be required. Boil from 5 to 7 minutes. At the end of this time, the liquid in the beaker must still be alkaline to litmus paper ; if not, add ammonia till alkaline and boil until the liquid becomes colourless. Let the precipitate settle for a few minutes, filter and wash the precipitate with hot water. When the washing has been sufficient to remove the sodium salts, ( ten washings will be sufficient ) dry the filter paper with the residue by placing it on 3 or 4 thicknesses of ordinary filter paper, transfer to a platinum crucible and heat gradually over a Teclu burner until the dioxide of manganese has changed into  $\text{Mn}_3\text{O}_4$ . Cool in a desiccator and weigh. Multiply the weight of  $\text{Mn}_3\text{O}_4$  by 0.7203 to get the weight of Mn.

## NOTES :—

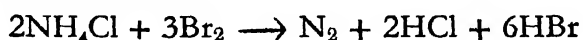
(1) The successful carrying out of the experiment depends on strict adherence to the details up to the point at which the iron is precipitated as basic ferric acetate.

(2) Solution of the steel in HCl is preferred to solution in  $\text{HNO}_3$  for the following reasons :— $\text{HNO}_3$  brings carbonaceous matter into solution in the form of nitrocompounds which interfere with a sharp separation of Mn from Fe. Hence solution in HCl with subsequent oxidation of  $\text{FeCl}_2$  by means of conc.  $\text{HNO}_3$  is effected. The carbon compounds pass off as gases when the steel is dissolved in HCl. If the iron is not in the ferric condition, separation of Fe from Mn is not possible. Ferrous acetate, unlike ferric acetate, is soluble in water and is not hydrolysed.

(3) Sodium carbonate solution is employed in place of ammonia to precipitate a very large part of the iron as hydroxide, as the  $\text{CO}_2$  liberated aids in the breaking up of  $\text{Fe}(\text{OH})_3$  into small flakes and the solution of the same in  $\text{FeCl}_3$ . The final precipitation of the small amount of iron in solution is accomplished by means of sodium acetate added at about  $80^\circ\text{C}$ . and in quantity just sufficient to precipitate the iron, thus preventing the formation of  $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2$ , and its hydrolysis, which result from a large addition of the reagent. Filtration must be proceeded with immediately after the solution has been made up to the mark and mixed. The process of filtration adopted here is what is known as 'fractional filtration' and is the same as was adopted in the gravimetric determination of sulphur in Pig Iron. The precipitate of basic ferric acetate is bulky. To wash it free from manganese salts is an operation which takes much time. Hence half the bulk of the solution, i.e. 500

ml. is taken for the actual precipitation of Mn as  $\text{MnO}(\text{OH})_2$ , thus dispensing with the necessity for washing the basic ferric acetate precipitate free from occluded Mn salt.

(4) The precipitation of Mn as  $\text{MnO}(\text{OH})_2$  is complete only when the solution from which it is precipitated is alkaline, or acid with a weak acid like  $\text{CH}_3\text{COOH}$ . Bromine reacts with ammonia and ammonium salts liberating acid, for the neutralization of which much sodium acetate is needed. Hence it is better to avoid, as far as possible, the introduction of ammonium salts into the solution from which Mn is to be precipitated. The reason for using  $\text{Na}_2\text{CO}_3$  and  $\text{NaC}_2\text{H}_3\text{O}_2$  in place of the corresponding ammonium salts will now be clear. The reaction with  $\text{Br}_2$  and  $\text{NH}_4\text{Cl}$  is as follows :—



(5) Conversion of  $\text{MnO}_2$  into  $\text{Mn}_2\text{O}_3$  is complete only at temperatures from  $950^\circ\text{--}1050^\circ\text{C}$ . . Either a muffle furnace or a Teclu burner must be used for the ignition of the precipitate.

(6) The procedure for the determination of Mn in Pig Iron is exactly similar. It is also adopted without modification for the determination of Mn in hematite ore, when a complete analysis of the same is required and when the short volumetric method for the determination of this element is not, therefore, available.

## EXPERIMENT 22.

### Determination of Manganese in Pig Iron and Steel.

#### Principle :—

Manganese which is present in Pig Iron in the form partly of  $\text{MnS}$  and partly of  $\text{Mn}_3\text{C}$  is changed to nitrate

by solution in dil.  $\text{HNO}_3$ . The nitrate thus formed is oxidized to permanganic acid by ammonium persulphate, a solution of silver nitrate being used as the catalytic agent. The permanganic acid is then titrated with a standard solution of sodium arsenite. From the amount of the arsenite solution used up, the percentage of Mn is calculated.

### Persulphate Method

1. **Dilute Nitric acid**:—S.G. 1.2. The same as in Experiment 13.

2. **Silver nitrate solution**:—Dissolve 1.3. gms. of the salt in 1 litre of distilled water.

3. **Ammonium persulphate solution**:—Dissolve 15 gms. of the substance in 100 ml. of cold distilled water. The solution does not keep well. It should therefore be prepared fresh each time it is required. Even the solid reagent decomposes if the container is not corked tightly.

4. **Sodium chloride solution**:—Dissolve 2 gms. in 1000 ml. water.

### Solutions required

5. **Standard Sodium arsenite**:—Approximately N/110. Weigh 0.5 gm. of pure arsenious oxide into a conical flask. Add about 2 gms.  $\text{Na}_2\text{CO}_3$  and 25 ml. water. Boil in a water bath. When completely dissolved, cool and make up to 1 litre. Fix the strength of the solution exactly by titrating against N/100  $\text{KMnO}_4$  solution.

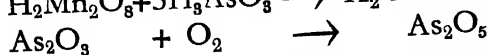
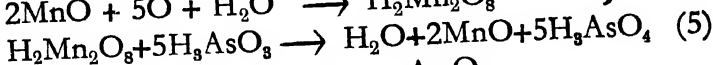
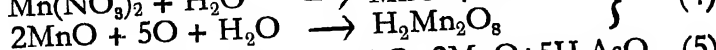
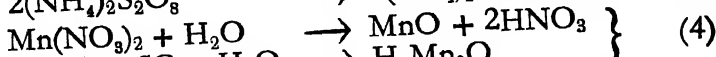
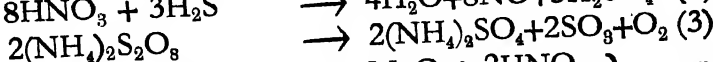
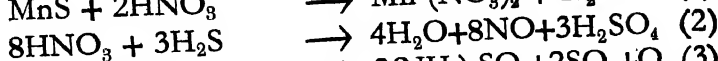
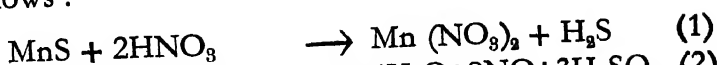
6. N/100  $\text{KMnO}_4$ . Take exactly 20 ml. of N/10  $\text{KMnO}_4$  prepared in Experiment 8, in 200 ml. measuring flask. Dilute to the mark with water. Mix well. To fix the strength of arsenite solution proceed as follows:—

pipette off 20 ml. of the  $N/100$   $\text{KMnO}_4$  solution into a 300 ml. conical flask. Add 15 ml. of dilute  $\text{HNO}_3$  s.g. 1.2. Add dropwise sulphurous acid or a 0.2% solution of potassium nitrite until decolorised, boil to expel the excess of sulphurdioxide or oxides of nitrogen, add 10 ml. silver nitrate solution, 15-20 ml. of the ammonium persulphate solution and boil 2-3 minutes in a water bath. Cool. Add 2-5 ml. of sodium chloride solution. Run the arsenite solution from a burette until the pink colour is discharged. Repeat twice. Let the mean value of the volume of arsenite solution used be 22.0 ml. Then, the strength of the arsenite is  $20/22. N/100$ . 1 ml. of this solution = 0.0001 gm. Mn.

**Procedure :—**Weigh 1 gm. sample into a 200 ml. Erlenmeyer flask, add 40-50 ml. of dil.  $\text{HNO}_3$  of s.g. 1.20. Heat in a water-bath or on a mush room top Bunsen burner until dissolved. Dilute somewhat with 20-30 ml. of cold distilled water. Filter off the graphite receiving the filtrate in a 200 ml. measuring flask. Wash the Erlenmeyer and filter paper 4 or 5 times, cool and make up to the mark. Thoroughly mix by shaking. Pipette off 20 ml. into a 200 ml. Erlenmeyer flask, add 5 ml. more of the same  $\text{HNO}_3$  (s.g. 1.20). Raise to a boil by heating in a water bath. Add 10 ml. of  $\text{AgNO}_3$  solution and after a minute or two, add 2 gms. of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (ammonium persulphate) dissolved in 10 ml. of water. Boil for about  $1/2$  minute after the colour fully develops or for 3 minutes after the addition of persulphate. Cool. Add 5 to 10 ml. of the 0.2%  $\text{NaCl}$  solution and titrate with standard  $\text{Na}_3\text{AsO}_3$  until the pink colour is just discharged. A white porcelain tile may be used in catching the exact end point or a sheet of white paper will equally serve the purpose. The titration is carried out after placing the flask on either of these, furnishing a white background.



The reactions relevant to the determination are as follows :—



$$1 \text{ litre } 0.1 \text{ N As}_2\text{O}_3 = \frac{\text{As}_2\text{O}_3}{40} = 1 \text{ litre } 0.1 \text{ N H}_2\text{Mn}_2\text{O}_8 = \frac{2\text{Mn}}{100}$$

**Record and Calculation of results :—**Weight of Pig Iron taken 1 gm.. Solution made to 200 ml.. 20 ml. solution corresponding to 0.1 gm. sample was used for oxidation to  $\text{H}_2\text{Mn}_2\text{O}_8$ .

$\text{H}_2\text{Mn}_2\text{O}_8$  required 5.6 ml. arsenite. Hence % Mn = 0.56.

In Works Laboratories the practice is to standardize the arsenite solution against a steel having a known percentage of manganese. Thus, if 0.1 gm. of a steel whose Mn content is 0.63% requires in the permanganic acid state 6.3 ml. of the arsenite solution, then 1 ml. of that solution = 0.1% Mn when 0.1 gm. of the sample is used for analysis.

NOTES :—

(1) The graphite in pig iron must be filtered off as otherwise it would cause a slight reduction of  $\text{H}_2\text{Mn}_2\text{O}_8$  and thus lower the value for Mn.

(2) The reactions must all be carried out in a water bath as overheating causes the decomposition of  $\text{H}_2\text{Mn}_2\text{O}_8$  formed.

(3) Even in the water bath, the permanganic acid must not be boiled for a prolonged time.

(4) The permanganic acid formed must be cooled to room temperature and then titrated ; otherwise, a slightly higher value will be obtained owing to the reoxidation of the reduced  $\text{H}_2\text{Mn}_2\text{O}_8$  by undecomposed  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  which may exist in solution.

(5) The addition of  $\text{NaCl}$  serves two purposes. It yields a white precipitate with the catalyst and this white background enables one to hit off the end-point sharply. The removal of  $\text{AgNO}_3$  by  $\text{NaCl}$  as  $\text{AgCl}$  prevents the re-formation of  $\text{H}_2\text{Mn}_2\text{O}_8$  by  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , which is added in excess and some of which remains undecomposed. This undecomposed persulphate will restore the pink permanganic acid if the catalyst is not removed out of the sphere of action by being thrown down as a precipitate. The liberal addition of solid sodium chloride instead of the solution of the strength specified has resulted in the disappearance of the permanganic acid colour. This is because of the formation of  $\text{HCl}$ .

(6) The procedure for Mn in steel is the same as above ; only filtration is omitted because there is no graphite in steel.

(7) The intensity of the colour produced by the sample of pig iron may be compared with the colour obtained by a sample of steel of known manganese content, similarly treated. If 100 ml. of the Pig Iron solution gives as intense a colour as 120 ml. of steel solution having 0.63% Mn, the weight taken in each case being the same, then the Mn content of the Pig Iron sample is  $\frac{0.63 \times 100}{120}$  or  $\frac{3.15}{6}$  or 0.525%. This method of determination of substances by comparison of colours is known as colorimetry.

(8) In alloy steels containing Cr, V and Co in

amounts less than 3%, 0.5% and 5% respectively, fairly accurate results for Mn may be obtained by finishing off a titration rapidly. Modified procedure when they are present in larger amounts, is dealt with in Experiment 23. Titanium, tungsten and molybdenum do not interfere.

(9) Sodium bismuthate is often substituted for ammonium persulphate for oxidizing Mn to its heptavalent condition. The precautions employed and the procedure followed are :—The nitric acid used for solution of the steel should be entirely free from Cl or HCl. 0.1 gm. of the steel is dissolved in 15 ml.  $\text{HNO}_3$  of 1.2 s.g. About 0.5 gm. of the bismuthate is added to oxidize the nitrated carbon compounds. Incidentally, permanganic acid is formed. The solution is boiled until this is decomposed and the precipitated  $\text{MnO}_2$  is dissolved by the addition of a few drops of a solution of  $\text{KNO}_2$  or sulphurous acid. The nitrous fumes or the excess of sulphurous acid are expelled by boiling. The solution is then thoroughly cooled and diluted with 40 ml. of cold water. To the cold solution, about 0.5 to 1.5 gm. of the bismuthate is added, shaken well for a few seconds and the permanganic acid formed filtered off quickly from the excess of undecomposed bismuthate through asbestos filter and titrated against the standard arsenite solution. Wash liquid is 3%  $\text{HNO}_3$  and should be free from  $\text{HNO}_2$ . The oxidant is the bismuth tetroxide which gets reduced to  $\text{Bi}_2\text{O}_3$ . The oxidation of Mn is effected by this reagent even at as low a temperature as  $0^\circ\text{C}$ ., a condition under which little or no chromium is oxidized when the same is present in the steel. But as ordinarily practised in Works' Laboratories, some chromium is oxidized and the interference due to the presence of this is avoided by proceeding with filtration and titration, after developing the colour, without any delay. The bismuthate method is not followed in the

Works' Laboratories in India, but it is a favourite method with English and American chemists and metallurgists.

(10) Ferrous sulphate solution is also used to reduce the permanganic acid; but as it changes its strength due to atmospheric oxidation, sodium arsenite solution is preferred.

(11) Ammonium persulphate decomposes, particularly during the monsoon months. It should therefore be kept in properly corked ( and waxed ) bottles. Large quantities of the solution of this substance in water should not be prepared and stocked on account of the liability to decomposition. The percentage purity of a sample may be ascertained as follows:—

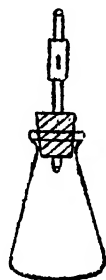


Fig. 9.

Weigh 0.3 gm. of the salt into a 300 ml. Erlenmeyer flask fitted with a Bunsen valve. Replace the air in the flask by carbondioxide. Add 30 ml. of a freshly titrated ferrous sulphate solution and 200 ml. of hot water. Shake well after closing the mouth of the flask. After 3 minutes, cool to room temp. and titrate the unused  $\text{FeSO}_4$  solution. From the volume of  $\text{FeSO}_4$  oxidized, calculate % purity of the salt. Example:—

30 ml. of  $\text{FeSO}_4$  solution consumed 30 ml. of 0.1 N  $\text{KMnO}_4$ .

30 ml. of  $\text{FeSO}_4 + 0.3$  gm. ammonium persulphate consumed 5 ml. of 0.1 N  $\text{KMnO}_4$ .

$$\text{Hence \% purity of the persulphate} = \frac{25 \times 0.01141 \times 100}{0.3} = 95.1.$$

For sketch of the Bunsen valve, see Fig 9. For description, see Expt. 62 b.

## EXPERIMENT 23.

### **Procedure for Manganese in Alloy Steels Containing Chromium, Vanadium and Cobalt.**

The method described for the determination of Mn in plain carbon steels by conversion into  $\text{HMnO}_4$  and titration with  $\text{Na}_3\text{AsO}_3$  requires modification when the above elements are present in the following amounts:—Cr more than 3%; V more than 0.5%; Co more than 5%. The two first elements register a high result for Mn because in the  $\text{H}_2\text{CrO}_4$  and  $\text{HVO}_3$  condition, to which they are oxidized by the persulphate, they have an oxidizing action on  $\text{Na}_3\text{AsO}_3$ ; the last has no such oxidizing action; but the pink colour caused by  $\text{Co}(\text{NO}_3)_2$  is indistinguishable from the pink colour caused by permanganic acid. Hence the end point cannot be hit off.

**Solutions required :—**The same as in Experiment 22 and  $\text{dil. H}_2\text{SO}_4$ . Pour 30 ml. conc.  $\text{H}_2\text{SO}_4$  into 90 ml. of water in a beaker.

**Principle of the modified method:—**Zinc oxide added to a solution of steel in  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  containing Cr as  $\text{Cr}_2(\text{SO}_4)_3$  and V as  $\text{HVO}_3$  precipitates them as  $\text{Cr}(\text{OH})_3$  and zinc vanadate respectively. The exact point at which the precipitation of Cr and V is complete becomes evident from the milkiness of the

supernatant liquid. After mixing, the precipitates are filtered off, and the manganese determined from the filtrate in exactly the same way as Mn in plain carbon steel.

**Procedure :—**Dissolve 0.1 gm sample in 10 ml. of 1.3  $\text{H}_2\text{SO}_4$  in a test tube 8"  $\times$  1" by gently heating directly on a Bunsen burner. Add 5 ml.  $\text{HNO}_3$  of s. g. 1.2, when solution is complete or nearly complete. Boil until brown fumes disappear. Make a thick paste of zinc oxide with water. Add this paste until the supernatant liquid is milky. Dilute with 25 ml. water. Filter and wash three times. To the filtrate ( about 50 ml. ) add 20 ml.  $\text{HNO}_3$  s. g. 1.2, heat in the water bath, add 10 ml.  $\text{AgNO}_3$  and then 10 ml. of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  ( 2gms. in 10 ml. water. ) When the colour is fully developed, that is, about 3 minutes after the addition of the persulphate, transfer to a cold water bath. When thoroughly cool, add 10 ml. of  $\text{NaCl}$  and run standard arsenite solution until the pink colour is discharged.

NOTES :—

(1) Chromium steels do not dissolve completely in dil.  $\text{HNO}_3$  of s. g. 1.2. Solution of the steel is effected in  $\text{H}_2\text{SO}_4$  ( 1 : 3 ). This acid has the effect of destroying organic matter and the subsequent separation of Mn by  $\text{ZnO}$  is complete. In the presence of carbonaceous or organic matter some of the manganese is carried down with the precipitate of Cr, Fe, etc. causing low results thereby. The addition of  $\text{HNO}_3$  converts the  $\text{FeSO}_4$  into  $\text{Fe}_2(\text{SO}_4)_3$ .

(2) Chromium salts are oxidized by ammonium persulphate to  $\text{H}_2\text{CrO}_4$ . This oxidizes arsenite.

(3) Co is not removed by  $\text{ZnO}$ . Most of it is removed by passing  $\text{H}_2\text{S}$  into a solution slightly acid with acetic acid. Co is precipitated as  $\text{CoS}$ . This is

filtered off. The filtrate is evaporated to low bulk ( 20 ml. ) with 10 ml. of conc.  $\text{HNO}_3$  and the usual operation for Mn is then carried out.

(4) When the amounts of chromium, vanadium and cobalt are less than those specified, the persulphate method is employed with the following modification :— The titration with the standard arsenite solution is performed rapidly. In that case, the reduction of  $\text{CrO}_3$  and/or  $\text{V}_2\text{O}_5$  by the arsenite is a minimum. .

( 5 ) When only vanadium is present in a steel but not chromium, excess of standard sodium arsenite solution is introduced and the excess titrated against standard potassium permanganate. The vanadic acid reduced by the arsenite is restored to its original condition by the permanganate solution. The difference between the volumes of  $\text{Na}_3\text{AsO}_3$  and  $\text{KMnO}_4$  which are of equal strength is a measure of the amount of Mn in the steel. The one precaution that is necessary is to add  $\text{KMnO}_4$  until the pink colour persists for at least one minute. This is because the vanadium gets oxidized only slowly.

(6) An alternative procedure for the determination of manganese in high chromium steels is based on the following principle :— Sodium bicarbonate solution precipitates chromium hydroxide from a mixture of solutions containing the sulphates of chromium, manganese and ferrous iron. The precipitate is filtered off and manganese is determined from the filtrate by oxidation with ammonium persulphate in the presence of silver nitrate. The procedure with the filtrate after reduction to low bulk by evaporation with dil.  $\text{HNO}_3$  of s. g. 1.2 is identical with that for manganese in plain carbon steels. Procedure for solution of the steel sample is as follows:—Dissolve 1 gm. of the steel sample contained in a 300 ml. Erlenmeyer flask covered by inserting a funnel in its mouth, in 20 ml. of dil.  $\text{H}_2\text{SO}_4$

(1:9). When action is complete, dilute to 100 ml. with boiling water. Add from a burette 8% solution of sodium bicarbonate until a permanent precipitate is formed, about 36 ml., and then 4 ml. more. Cover the flask and boil for 1 minute and let the precipitate settle. Filter rapidly and wash residue four or five times with hot water. Heat filtrate to boiling and oxidize by adding about 12 ml. of  $\text{HNO}_3$  of s.g. 1.4, in small quantities at a time.

Evaporate to about 25 ml., transfer to a 200 ml. measuring flask, rinse three or four times with water and make up the solution to the 200 ml. mark with distilled water. Mix thoroughly. Pipette off 20 ml. into a conical flask and complete the determination of manganese as in plain carbon steel.

## EXPERIMENT 24.

### Determination of Carbon in Pig Iron, Steel and Ferro-Alloys by Direct Combustion.

**Principle:**—When a current of pure, dry oxygen is passed over any of the above materials in suitable physical condition, drillings or powder, heated to  $1100^\circ\text{C}$ . in an electric furnace, the non-metallic elements carbon, sulphur and phosphorus are converted into oxides which are gaseous while the metallic elements are converted to oxides which are solid. The gaseous products consisting of  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{P}_2\text{O}_5$  and excess of oxygen are collected in a burette, very similar to that of Hempel for the analysis of gases ( Experiment 88 ) and connected to a levelling bottle, with water as the confining medium. Owing to their high solubility  $\text{SO}_2$  and  $\text{P}_2\text{O}_5$  readily dissolve in the water which is in the burette and the levelling bottle. The reading of the



burette, when the levels of water in it and the levelling bottle are the same, gives the volume of  $\text{CO}_2$  and the excess of oxygen. This mixture is then passed into an absorption bulb filled with caustic potash solution. The residual gas is transferred back to the burette and its volume measured at the temperature of the water in the jacket surrounding the burette and at the Laboratory pressure. The difference between the two readings is the volume of  $\text{CO}_2$ . From this volume the weight of carbon in the material is calculated.

**Solution Required :—**Dissolve 100 gms. of potassium hydroxide in 200 ml. water.

**Procedure :—**

The apparatus used is shown in Fig. 10 b.

Weigh 1 gm. of steel drillings and spread uniformly on a layer of dead burnt magnesite contained in a nickel boat, previously heated for several hours in the furnace to convert any carbon that it may contain to  $\text{CO}_2$ . Sweep out  $\text{CO}_2$  formed by passing oxygen. Introduce the boat into the unglazed porcelain tube S shown in the figure. Quickly close the mouth of the tube and pass a rapid stream of oxygen from the gas holder, gradually lowering the levelling bottle from the highest point to which it has been raised to the lowest position on the rod along which it is slid. When the burette in which the gases collect is nearly full, stop the supply of oxygen. Turn the two-way stop-cock suitably so that the products of combustion are confined in the burette and pass neither out into the open air nor into the absorption bulb. Withdraw the nickel boat from the tube S with the help of the stout bent steel wire and receive it in the asbestos-tray provided.

Adjust the levels and note the reading on the burette. Turn the two-way cock so as to put the burette and the absorption bulb in communication with each other. Pass the gases over into the absorption bulb by raising the levelling bottle. Take back the gases into the burette by lowering the levelling bottle. Repass and repeat the operation three or four times until the residual-gas volume is constant. Note the temperature of the water in the jacket tube surrounding the burette in which the products of combustion collect and the atmospheric pressure. Reduce the volume obtained to standard conditions of temperature and pressure. after allowing for aqueous tension. From the equation



calculate the weight of carbon that will yield the volume of carbon dioxide obtained. Hence obtain the percentage of C in the steel.

NOTES :—

(1) The combustion of the carbon in the apparatus described is finished in 3 minutes. On account of the great ease of manipulation and the rapidity of combustion, this method has come into use very largely in all Steel Works' Laboratories and especially at the Laboratories where control tests on carbon are conducted during the process of refining of the pig iron into steel.

(2) The results obtained are accurate with all classes of material. It has not the limitations of the colour method of carbon determination described in Experiment 25.

(3) It has a great advantage over the method of absorbing  $\text{CO}_2$  in KOH solution and weighing it, in that elaborate precautions have not to be taken to free the mixture of gases from  $\text{SO}_2$  and  $\text{P}_2\text{O}_5$  and to ensure

that the same amount of dryness exists in the products entering and leaving the absorption bulb. There are no fragile parts to handle.

(4) Any  $\text{CO}_2$  that may be present in the oxygen supply must be removed by passing through KOH solution contained in a gas washing bottle and the particles of KOH solution likely to be carried by the rapid stream of oxygen, removed by passing through conc.  $\text{H}_2\text{SO}_4$  contained in a second gas washing bottle.

(5) Alundum boats and alundum powder may take the place of nickel boat and dead burnt magnesite respectively. The layer of alundum or magnesite helps the removal of the oxide from the boat. Without this layer, the removal is difficult and the boat will be rendered unfit for use after 4 or 5 runs. With a layer of one of the materials, 70-100 runs may be made with one nickel boat. Unglazed porcelain boats are also used. With care, they will serve for 6-10 runs each. They must not be allowed to drop from a height in withdrawing them in the red hot condition from the combustion tube. The asbestos tray must be held very close to the mouth of the tube S when withdrawing the boat. The same lining materials will serve in this case also.

(6) The silica tubes which may be substituted are costly and great care must be taken to preserve their life. A spattering of the oxide of iron to the wall of the silica tube leads to the formation of fusible ferrous silicate followed by cracking of the tube. The spattering of the oxide and the consequent damage to the silica tube may be prevented by putting a loose sheath of the same material as the boat on it and then introducing it into the silica tube. Unglazed porcelain tubes impermeable to gases and of the brand known as

'Pythagoras' are manufactured in India by Messrs. Burn & Co, Raniganj.

(7) In routine work, calculation is facilitated by reference to Table No. 1. It must be borne in mind that the table has been drawn up, calculating in the manner described in the Example ( See below ).

(8) In the case of materials having more than 1% C, not more than 0.2 gm. sample should be taken. This is because of the fact that the capacity of the burette with the cylindrical bulb is only about 200 ml. and that to sweep out the  $\text{CO}_2$  from the combustion tube nearly 15-20 times its volume of oxygen is necessary. In the case of materials of higher carbon content than 1%, the volume cannot be accommodated in the burette with the cylindrical bulb. As the latter is ungraduated, there will be a further difficulty in measuring the residual gas after the absorption of  $\text{CO}_2$  by KOH solution.

(9) The oxidation of the carbon in pig iron and some of the ferro alloys like ferro-chrome, ferro-manganese is helped very much by the addition of about 0.1 gm. of lead peroxide to the material whether in the form of powder or drillings.

(10) The heating elements used are two carborundum rods connected in series. The voltage of the electric current supply required is 220 D.C. The maximum current required to maintain the necessary temperature of  $1050^\circ\text{C}$  to  $1150^\circ\text{C}$ . is 4.5 amperes. This is reached within about one hr. after the current is switched on, provided the voltage of the supply line is 220. In case the voltage drops, the necessary temperature will not be attained. But it is possible to make carbon determination on plain carbon steels and pig irons if the temperature does not fall below  $900^\circ\text{C}$ .

(11) With use the carborundum rods get oxidized. The result is the formation of a layer of silica on them. With the formation of this layer, the conductivity drops and the required temperature is not attained. By employing current at a higher voltage, the rods may be made to give further service.

(12) Resistance wires have not the life that carborundum rods have. Hence the use of the latter in the combustion furnace.

(13) Oxygen required for this experiment is obtained from a cylinder of the compressed gas supplied in steel cylinders. These are available in capacities ranging from 10c. ft. to 100c. ft. of the gas at atmospheric pressure. The pressure to which the gas is compressed is of the order of 1500 lbs. per sq. inch. The gas cannot therefore be drawn directly from the cylinder for this experiment unless it is fitted with a device known as the regulating and the reducing valve. This permits of the gas being drawn at a pressure varying from 5 lbs. per sq. inch to 45 lbs. per sq. inch. Even when this device is available, it is necessary to draw the supply of oxygen for the combustion from a gas-holder. The Pepys holder is the one in common use. That in use in the College has a capacity of about 30 litres of oxygen at atmospheric pressure. Fill it with oxygen from the cylinder as follows:—First fill it with water. Admit water from the reservoir *R* at the top into the holder *G* by opening the cock *c*. When completely filled with water, it will flow out from the tap *t*. Have at least a column of water 6 inches in *R* when *G* has been filled. Close the cock *c* and the tap *t*. Unscrew the cap *C*, fitting the top of the soldered tube *st* near the lower end of *G*. Introduce a piece of rubber-tubing to a depth of about half of an inch into the water column in *st*. Connect the other end of the rubber tubing to *P*, the

metal tube from which the gas from the oxygen cylinder *C* issues on opening the valve *V*, with the special key supplied with the cylinder. To open *V* give a few gentle strokes to the key after engaging it with *V*, with a wooden mallet. Turn the handle *H* anticlockwise half to one turn. *G* must be placed near a sink so that, as the gas fills it, water empties into the sink. In 5 to 10 minutes after opening *V* and *H*, *G* will be filled with the gas. The level of water in the glass-gauge fitted to *G* indicates how much of *G* has been filled with the gas. To draw gas from *G* for the combustion experiment all that is necessary is to run water from *R* through the cock *c*, to open the tap *t* and to connect it by means of a piece of rubber-tubing to the wash-bottle containing caustic potash solution. The cylinder, the gas holder and the wash-bottles are all shown in Fig. 10 a .

(14) Before starting an experiment, the student is advised to acquire a little practice in handling the apparatus by passing oxygen through the combustion tube, collecting the gas in the burette, measuring its volume, passing it into the absorption pipette, transferring the residual gas back into the burette and ultimately discharging it into the air by suitably turning the two-way cock and raising the levelling bottle until the glass float provided in the burette prevents the escape of liquid by any inadvertent raising too much of the levelling bottle.

(15) There are also glass floats provided in the caustic potash absorption pipette. Sometimes gas bubbles get entrapped in the pipette. By a quick lowering of the levelling bottle, such entrapped gas bubbles may be dislodged and transferred to the burette.

(16) The only way to assure oneself that the combustion of the sample has gone right is to press

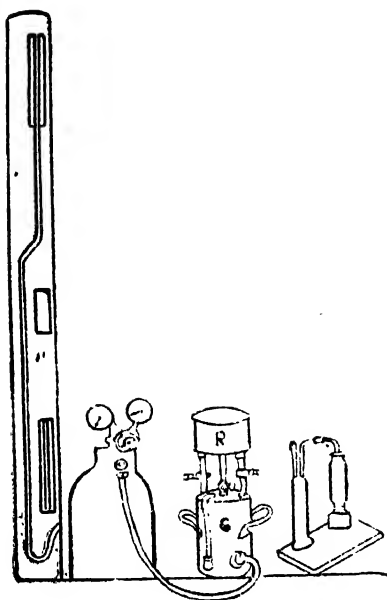


Fig. 10 a.

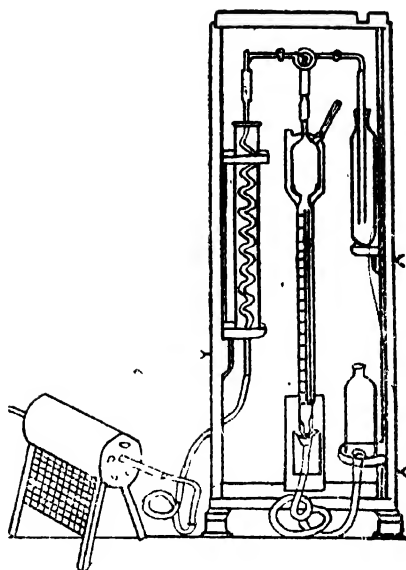


Fig. 10 b.



Fig. 10 c.

between the fingers or to gently hammer on a small one inch square anvil block the burnt drillings. If they crumble to powder without flattening, the combustion has gone right.

(17) To enable readings on the burette to be taken with greater ease, water, acidulated with one or two ml. of dilute sulphuric acid of s.g. 1.2 and to which a few drops of methyl orange have been added, is used as the confining liquid in the burette and the levelling bottle.

(18) One-holed rubber corks are used for closing the inlet and the outlet end of S. To avoid the softening of the rubber corks by the heat radiated from the hot part of S, it is desirable to have 6-8 inches of tube projecting from either end of the furnace. The total length of S must be about 24 inches. About  $\frac{3}{4}$  inch is a suitable diameter for S.

(19) A solid absorbent known as 'ascarite' is in regular use in Iron and Steel Works' Laboratories in the U. S. A. for the absorption of  $\text{CO}_2$ . The 'ascarite' container is weighed before and after an experiment. From the increase in weight, the percentage of carbon is calculated. But, as already pointed out, this method requires elaborate precautions for the elimination of  $\text{P}_2\text{O}_5$  and  $\text{SO}_2$  and is not as rapid as the volumetric one.

(20) Substances like red lead, lead dioxide, etc. which are used to help the combustion of ferroalloys and which are known as 'accelerators', will give a blank, (i. e.) a small volume of  $\text{CO}_2$ . This blank must be determined and allowed for. The same weight as is used in a blank run must be used in the sample run. Similarly, the dead-burnt magnesite will give a blank. This must be determined and allowed for.



**Example :—**

Weight of sample 1 gm.

Reading of the burette after collecting  $\text{CO}_2$  and  $\text{O}_2$  000

Reading after absorption of  $\text{CO}_2$  120

120 divisions = 12 ml.

Volume of  $\text{CO}_2$  = 12 ml.

Temperature of the water in the tube jacketing the burette =  $27^\circ \text{C}$ .

Barometric pressure = 760 mm.

Aqueous tension at  $27^\circ \text{C}$ . = 26.5 mm

22.4 litres of  $\text{CO}_2$  at N.T.P. result from the combustion of 12 gms. of carbon.

$$\frac{10 \times 273 \times (760 - 26.5)}{300 \times 760} \text{ or } 10.54 \text{ ml. } \text{CO}_2 \text{ at}$$

N.T.P. will result from  $\frac{10.54 \times 12}{22400}$  gms. of carbon.

1 gm. of steel sample contains  $\frac{10.54 \times 12}{22,400}$  gms. of carbon.

$$100 \text{ gms. steel sample contain } \frac{10.54 \times 12 \times 100}{22,400}$$

or 0.565 gm. carbon.

Percentage of C in the steel = 0.565

In routine work, the following rule is observed :—

Multiply the number of ml. of  $\text{CO}_2$  obtained in an Experiment by the factor corresponding to the observed temperature and pressure in Table No. 1. Divide the product obtained by 20 and the quotient so obtained represents the percentage of carbon in the material, when 1 gm. of sample has been taken for analysis.

Thus in the example above given the percentage of carbon is :

$$\frac{12 \times 0.940}{20} \text{ or } 0.565$$

TABLE No. 1.

Temp. °C	Pressure expressed in mm. of mercury				
	740	745	750	755	760
15	·973	·980	·987	·994	1·00
16	·969	·976	·983	·990	·996
17	·964	·971	·978	·985	·991
18	·960	·967	·973	·980	·987
19	·955	·962	·968	·975	·982
20	·957	·958	·964	·971	·977
21	·946	·953	·959	·966	·972
22	·941	·948	·954	·961	·967
23	·936	·943	·949	·956	·962
24	·931	·938	·944	·951	·957
25	·926	·933	·939	·946	·952
26	·921	·928	·934	·941	·947
27	·917	·923	·929	·936	·942
28	·912	·918	·924	·931	·937
29	·906	·913	·919	·926	·932
30	·901	·908	·914	·921	·927
31	·896	·902	·908	·916	·927
32	·891	·897	·903	·910	·916
33	·885	·891	·897	·905	·910
34	·880	·886	·892	·899	·905
35	·874	·880	·886	·894	·899
36	·869	·875	·881	·888	·894
37	·863	·869	·875	·882	·888
38	·856	·863	·869	·875	·882
39	·850	·856	·862	·869	·875
40	·844	·850	·856	·863	·869
41	·837	·843	·849	·856	·862
42	·831	·837	·842	·850	·857
43	·824	·831	·836	·843	·851

## EXPERIMENT 25.

## THE DETERMINATION OF CARBON IN STEEL

## By the Colorimetric Method (Eggertz's Method)

**Principle :—**When steel is dissolved in dilute nitric acid, the carbon present in the combined condition forms a nitro-compound which is brown-coloured. The intensity of the colour is proportional to the amount of carbon present.

**Solution required :—**Dilute  $\text{HNO}_3$  of s.g. 1.2. Mix 100 ml. of the purest conc.  $\text{HNO}_3$  obtainable with 120 ml. of distilled water.

**Procedure :—**

Weigh 0.1 gm. of a standard steel ( i. e. steel with a known percentage of carbon ) into a clean dry test tube. Mark this 'S' with a glass-marking pencil. Similarly weigh 0.1 gm. of the sample under examination into a second clean, dry test tube. Add to each 2 ml. of  $\text{HNO}_3$  s.g. 1.2 using a 2 ml. pipette for the purpose. When the brisk action has slowed down, place them in a bath of boiling water and heat for 10 minutes at the end of which time the drillings will have completely dissolved. Remove the test tubes to a cold water bath. Transfer the solution in the tube marked 'S' into a graduated colour comparison tube of 30 ml. capacity which is also marked 'S'. Rinse the test tube with 1 ml. of water. Transfer the rinsing to the same graduated tube. Repeat this 2 or 3 times. Make up to a definite volume with distilled water and mix well by shaking. If the percentage of carbon in the standard is 0.60, dilution to 20 ml. is convenient. Similarly, transfer the contents of the tube in which the sample was dissolved to a second graduated tube, rinse and mix well. Hold the tubes against a closed window, one of the glass panes of which is covered by a filter-paper. The

tubes are held against the white back-ground so improvised. If the colour of the sample is darker, add water, from a burette or other device, in small quantities at a time, mix well and compare. Repeat until the colour of the sample exactly matches that of the standard. If the sample is lighter, proceed with the standard in the manner described above until the colours are matched. Change the relative positions of the two tubes when making a test, that is to say, what was to the right is shifted to the left. To most people, things to the left appear darker and so the change of the positions of the comparator tubes helps greatly in judging correctly.

### Example of Calculation :—

Let the Standard Steel contain 0.60% carbon and let the volume of solution in the graduated tube S be 20 ml. If the volume of solution in the tube with the sample which matches the colour of the Standard is 19 ml., then, the percentage of carbon in the sample is

$$\frac{0.60}{20} \times 19 \text{ or } 0.57$$

### Notes on the Process :—

1. The nitric acid used for dissolving the steel must be the purest obtainable. Traces of chlorine or hydrochloric acid destroy the colour.
2. Prolonged boiling even in the water bath tends to make the colour paler. Hence more than 10-15 minutes' boiling is injurious.
3. The Standard Steel must have approximately the same percentage of carbon as the sample under test.
4. Both the Standard and the sample must have been made by the same method of manufacture; that is to say, basic open hearth steel must be compared with a

Standard also made by the basic open hearth process, acid Bessemer steel with acid Bessemer Standard and so on.

5. The standard and the sample must have undergone the same heat-treatment and the same mechanical treatment.

6. The conditions under which the Standard and the sample are treated must be identical, that is to say, the same volume of acid must be used for the same quantity, and both must be boiled for the same length of time in test tubes of the same size. In deciding what weights of steel, standard and sample, are to be used in the several cases that arise, the following table will be helpful.

(From Arnold and Ibbotson's 'Steel Works Analysis')

%Carbon in steel (Approximately)	% carbon in Standard	Weight of steel in gms.	Size of tube in inches.	Volume of acid of s.g. 1.2 in ml.
1.3 to 1.7	1.50	0.05	$6 \times \frac{1}{4}$	3
1.1 to 1.3	1.20	0.05	„	3
0.8 to 1.1	0.90	0.10	„	4
0.4 to 0.8	0.60	0.10	„	3
0.2 to 0.4	0.30	0.10	„	2
0.1 to 0.2	0.15	0.30	$6 \times 1$	1

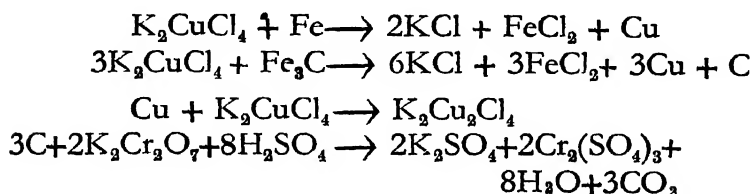
7. The method is not applicable to alloy steels containing large percentages of chromium, nickel and copper, as the nitrates of these metals give coloured solution, completely masking the colour due to the formation of the nitro compound.

#### EXPERIMENT 25 A.

#### Determination of Total Carbon in Pig Iron ( Ibbotson's Method )

**Principle** :—When pig iron drillings are treated with a solution of potassium cupric chloride in water,

the iron displaces copper from solution and the carbon existing in the iron both in the free and the combined form is obtained as a residue. This residue is filtered off through asbestos and treated at about  $130^{\circ}\text{C}$ . with a measured excess of standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution in 50%  $\text{H}_2\text{SO}_4$  whereby the C is oxidized to  $\text{CO}_2$ . The unused amount of the dichromate is found by titration with standard  $\text{FeSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $6\text{H}_2\text{O}$  solution. From the amount of dichromate used, the amount of carbon is calculated. The reactions that take place during the several stages are :—



### Solutions required :—

1. a. 50% sulphuric acid.  
To 550 ml. of water add gradually 270 ml. of conc.  $\text{H}_2\text{SO}_4$  ( s.g. 1.84 ).
- b. Dil  $\text{H}_2\text{SO}_4$  of s.g. 1.18. The same as in Expt. 13.
2. Potassium cupric chloride solution. Dissolve 300 gms. of the double chloride in water containing 75 ml. of  $\text{HCl}$  of s.g. 1.2 and dilute to 1 litre with water.
3. Standard Potassium dichromate solution :—  
Dissolve 19.6 gm. of the pure salt in 50% sulphuric acid and make up to 1 litre exactly with the same acid. The solution is  $2\text{N}/5$  strong. 100 ml. of this will be required for one determination, using 1 gram of pig iron.
4. Standard Ferrous ammonium sulphate solution.  
Dissolve 156.8 gms. of the salt in water and make up

to 1 litre with 50%  $\text{H}_2\text{SO}_4$ . About 75 ml. of the solution will be required for each determination.

5. 1 litre of a solution of calcium chloride containing 1010 gms of the anhydrous salt. This solution has a boiling point of about  $130^\circ\text{C}$ .

### Procedure :—

Weigh 1 to 1.5 gms. of pig iron drillings into an Erlenmeyer flask of 250 ml. to 350 ml. capacity. Introduce at the rate of 100 ml. of the potassium cupric chloride solution per gram of drillings into the flask containing the drillings. Fit it with a two-holed cork and connect as shown in Fig. 11 with the Bunsen filter pump and allow the process to go on for at least

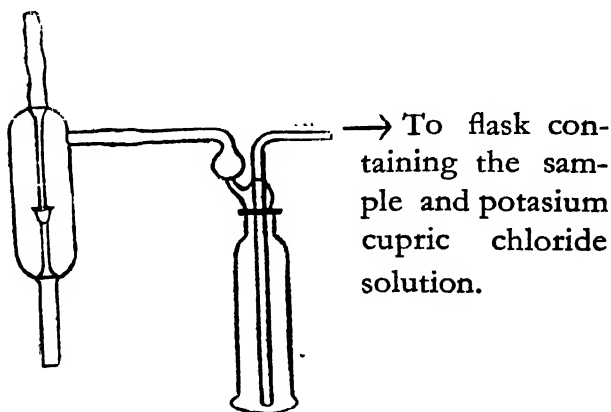


Fig. 11

4 hours. Filter through a Gooch crucible containing a felt of asbestos. Wash, until free from iron, the flask and the residue on the asbestos felt, with hot dilute sulphuric acid of s.g. 1.18. Care must be taken to see that all the residue in the flask is transferred to the asbestos felt. When free from iron, the felt with the residue is lifted off the crucible and placed in a beaker of 150 ml. capacity. Any residue adhering to the sides

of the Gooch crucible may be wiped with moist asbestos and the same placed in the beaker. 100 ml. of the *dichromate sulphuric acid mixture*. ( i.e. ) solution No. 3. is added to the beaker by means of a pipette. The beaker with the contents is heated in a bath of calcium chloride solution (temperature about  $130^{\circ}\text{C}.$ ) for about an hour. Transfer the contents of the small beaker to a 500 ml. beaker, and rinse it with cold water. Cool to room temperature. Run from a burette 70-100 ml. of the standard ferrous ammonium sulphate solution (No. 4) into the beaker and titrate the excess of it with the dichromate solution, using potassium ferricyanide as external indicator. From the amount of dichromate solution used, calculate the percentage of total carbon in the sample of pig iron.

**Example:—**

1.5 gms. of pig iron were treated with 150 ml. of  $\text{K}_2\text{CuCl}_4$  solution. The residue was filtered off through asbestos felt on a Buchner funnel and heated for  $2\frac{1}{2}$  hours with 50 ml. of  $2\text{N}/5 \text{ K}_2\text{Cr}_2\text{O}_7$  in a beaker of 150 ml. capacity, placed in a bath of calcium chloride solution boiling at  $130^{\circ}\text{C}.$  67.6 ml. of  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  were added to the cold contents of the beaker. The excess of this solution required 45.1 ml.  $2\text{N}/5 \text{ K}_2\text{Cr}_2\text{O}_7$ .

$$\text{Total volume of } 2\text{N}/5 \text{ K}_2\text{Cr}_2\text{O}_7 = 95.1 \text{ ml.}$$

$$\text{Volume of FeSO}_4 = 67.6 \text{ ml.}$$

67.6 ml.  $\text{FeSO}_4 = 46.5 \text{ ml. K}_2\text{Cr}_2\text{O}_7$ , as ascertained by a separate titration.

Hence, volume of  $\text{K}_2\text{Cr}_2\text{O}_7$  used up in oxidizing the carbon in the iron is  $95.1 \text{ ml.} - 46.5 \text{ ml.}$  or 48.6 ml.

$$1 \text{ ml. of } 2\text{N}/5 \text{ K}_2\text{Cr}_2\text{O}_7 = 0.0012 \text{ gm. carbon.}$$

$$48.6 \text{ ml. } \quad \quad \quad = 48.6 \times 0.0012 \text{ gm. carbon.}$$

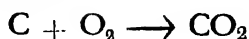
$$1.5 \text{ gms. pig iron contain } 48.6 \times 0.0012 \text{ gm. C}$$



$$100 \text{ gms.} \quad \frac{48.6 \times 0.0012 \times 100}{1.5}$$

or 3.888% C.

From the equation



it follows that 1 litre of 2N/5 contains

$\frac{2 \times 12}{5 \times 4}$  i. e. 6/5 gms. of carbon, supposing it to exist suspended in water.

1 litre 2N/5  $\text{K}_2\text{Cr}_2\text{O}_7$  = 1 litre 2N/5 C  
 or 1 ml. 2N/5 „ = 0.0012 gm. C.

A duplicate run on the same sample yielded 3.792% carbon.

The approximate percentage error is 2.25, which in a determination of this nature is permissible. (The correct percentage has been assumed to be 3.888.)

The relation between the dichromate and the ferrous ammonium sulphate solution as obtained by the separate titration referred to above, was:—

	2N/5 $\text{K}_2\text{Cr}_2\text{O}_7$	$\text{FeSO}_4, (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
Final reading	14.4	21.3
Initial reading	0.1	0.5
Volume used	15.3	20.8

NOTES:—

(1) The presence of HCl in potassium cupric chloride solution has a beneficial effect on the quick separation of carbon. Cuprous chloride which is a product of the reaction will, if not dissolved by HCl, interfere with the attack on iron, by forming a protective layer on the drillings.

(2) Asbestos and not filter paper is to be used for filtration of the carbonaceous residue. The dichromate

-sulphuric acid will oxidize the filter paper and the carbon percentage obtained on the sample will be higher than the true value.

(3) Washing with dil.  $\text{H}_2\text{SO}_4$  is necessary to remove ferrous salts. These, if present, will vitiate the accuracy of the results by reacting with the dichromate solution.

(4) 50%  $\text{H}_2\text{SO}_4$  is preferred to acids of other concentration as this acid alone has the maximum effect in hastening the oxidation of the carbon by the dichromate. At  $130^\circ\text{C}$ , the reduction of the dichromate by this acid is negligibly small; that is to say, no chromium sulphate  $\text{Cr}_2(\text{SO}_4)_3$  is formed with the 50% acid.

(5) The spotting plate becomes very serviceable even when not of the best make by coating it with a layer of paraffin wax. A drop of the solution to be tested when placed on the plate thus coated does not spread. After the test is over, it is easily washed, no stains being left.

(6) The following table from Mellor's 'Inorganic Chemistry' shows the concentrations of chloride solutions and the corresponding boiling points:

No. of gms. of anhydrous $\text{CaCl}_2$ in 100 gms. of $\text{H}_2\text{O}$	11.5	25	101	222
Boiling points in Centigrade degrees	102	105	130	160

(7) This method is becoming obsolete. It is described here in order that small laboratories, attached to Foundries, which cannot afford expensive equipment, like the Strohlein apparatus, may carry out, with reasonable accuracy and rapidity, the determination of total carbon.

## EXPERIMENT 26.

**Determination of Graphite in Pig Iron.**

Carbon exists in Pig Iron partly in the free or uncombined condition and partly in the combined condition as  $\text{Fe}_3\text{C}$ . The two forms are determined separately, as these give an indication of the softness or hardness of the metal and therefore its suitability or otherwise for the foundry.

**Determination of Graphite :—**

**Principle :—**When a sample of pig iron is dissolved in nitric acid, the combined carbon goes into solution yielding a nitro-compound while the graphite carbon is left unattacked. This is filtered off through tared filter papers which are dried at  $100^\circ\text{C}$ . The increase in weight of one of the papers over the other gives the amount of graphite in the pig iron.

**Solutions required :—**

1. Dilute  $\text{HNO}_3$  s.g. 1.135. Pour 100 ml. of conc.  $\text{HNO}_3$  into 200 ml. water in a bottle. Mix well by shaking.
2. Dilute  $\text{HCl}$ . Mix 10 ml. conc.  $\text{HCl}$  with 20 ml. water.
3. 5% ammonia. Mix 10 ml. of ammonia of s.g. 0.88 with 45 ml. water.

**Procedure :—**

Dissolve 1 gm. of pig iron in a 150 ml. beaker in 50 ml. of  $\text{HNO}_3$  of 1.135 s.g.. Keep at a gentle boil for 1 hour on the hot plate, covering the beaker with a cover glass. Remove from the hot plate, filter through the tared filter papers which have been fitted to a funnel, wash with cold water, hot dil.  $\text{HCl}$  (solution 2), cold water, 5%  $\text{NH}_4\text{OH}$  solution and finally with hot water. Spread the papers on a watch glass, and dry in

an air oven at  $100^{\circ}\text{C}$ . When the papers become dry, ( this will take about 1 hour ), cool them in a desiccator and find the increase in weight of the paper with the deposit of carbon, over the other and calculate the percentage.

NOTES:—

( 1 ) Nitric acid of the specific gravity specified does not lead to the separation of silica in a gelatinous form which makes filtration tedious.

( 2 ) Even when using acid of this s.g., it is necessary to boil gently and prevent the concentration of acid by covering with a cover-glass. A tall narrow beaker is to be preferred to one of the same capacity but with a broad bottom, as solution is effected in the former without separation of silica.

( 3 ) If the filtration consumes much time due to the separation of silica in a gelatinous form, a real difficulty arising in the case of very grey pig irons, the experiment must be started over again and a few drops of hydrofluoric acid added after the pig iron drillings have dissolved in  $\text{HNO}_3$ . After such treatment the filtration of the solution is considerably facilitated.

( 4 ) The combined carbon in the pig iron may be converted into solid, liquid or gaseous hydrocarbons on boiling with dil.  $\text{HNO}_3$ . The non-volatile hydrocarbons are soluble in alkalis, alcohol or ether. In very accurate work, it is desirable to give a wash with all of these liquids in succession. 5% ammonia serves for the alkali wash. When ether wash is made, it must be followed by cold water wash until the ether is removed.

( 5 ) To be very accurate, the filter-paper with the deposit of carbon must be burned in a platinum crucible

in a muffle furnace and the weight of the small amount of silica deducted from the weight of residues obtained by drying in the air-oven at  $100^{\circ}\text{C}$ .

( 6 ) In preparing tared filter papers, they must not be held with the fingers at the time of cutting them with a pair of scissors. They must be handled with a pair of forceps. Moisture in the hands is absorbed and the adjustment to equality of weights is never attained in consequence.

( 7 ) Dil. HCl. of s.g. 1.12 may be employed with advantage for dissolving white pig iron high in combined carbon. This acid, unlike  $\text{HNO}_3$ , does not lead to the separation of sulphur along with the graphite carbon. When dealing with pig irons made from titaniferous iron ore, dil.  $\text{HNO}_3$  must be employed, as HCl will not dissolve the titanium carbide present in those irons.

( 8 ) An alternative method for the determination of graphitic carbon consists in dissolving the pig iron drillings in dil.  $\text{HNO}_3$  as above, filtering off the graphite through asbestos felt on a perforated porcelain disc or plate and burning off the residue, after drying, in the combustion apparatus described in Experiment 24.

**Example :—**

Weight of pig iron	=1.0000 gm.
Weight of graphite + $\text{SiO}_2$ + water tenaciously adhering to $\text{SiO}_2$ at $100^{\circ}\text{C}$ .	=0.0356 gm.
Weight of residue on burning the deposit	} =0.0050 gm.
Weight of graphite	
Percentage of graphite	=3.06.

## EXPERIMENT 27. .

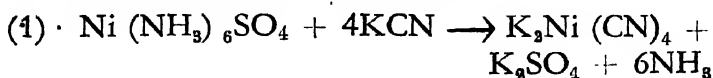
# Determination of Nickel in a Sample of Nickel-Steel.

## ( The Cyanide Method. )

### Principle :—

When a solution of potassium cyanide is added to nickel sulphate solution, a precipitate appears first which dissolves when an excess of it is added. The indication of the point at which the precipitated nickel cyanide has completely been dissolved by KCN is obtained with the help of AgI which remains suspended in the liquid that is being titrated. The disappearance of the turbidity due to silver iodide marks the point at which  $\text{Ni}(\text{CN})_2$  has been completely dissolved by KCN. This reaction also takes place between a ferric or a ferrous salt and KCN. Either the removal of these salts or the interference caused by these salts is therefore a necessity. Copper and cobalt salts also interfere with the method as they react with KCN in a manner similar to Ni salts. As these metals are not present at all, or, are not present in more than traces in ordinary steels, no provision need be made for their removal. For the removal of iron, the basic acetate separation is available but as it is lengthy, the interference is prevented by the addition of a large amount of citric acid and ammonia leading to the formation of un-ionised iron citrate.

The reactions that take place are :—



**Solutions required :—**

- (1) Dil. HCl s.g. 1.1. The same as in Expt.No. 13.
- (2) Dil.  $\text{HNO}_3$  s.g. 1.2    „    „    „    „    „    „
- (3) Dil.  $\text{H}_2\text{SO}_4$ . Pour 30 ml. conc.  $\text{H}_2\text{SO}_4$  into '90 ml. water.
- (4) 2% KI solution. Dissolve 2 gms. in 100 ml. water.

(5) Standard Silver Nitrate solution. Dissolve 2.9 gms. of the salt in water and make upto 500 ml. exactly.

(6) KCN solution. Dissolve 5 gms in 500 ml. water Add 1 gm. KOH. Dilute to about 1000 ml.

**Procedure :—**

Weigh 1 gm. steel drillings into a 150 ml. beaker. Add 20 ml. dil. HCl (s.g. 1.10) and place on the hot plate. When dissolved, add 10 ml. of dil  $\text{HNO}_3$  (s.g. 1.2) to oxidize the iron to the ferric state. Evaporate to half the bulk. Remove from the hot plate, add 30 ml. of sulphuric acid (solution 3). Transfer the contents to a large beaker (600 ml.). Introduce 12 gms. of powdered citric acid. Stir until dissolved. Add ammonia until slightly alkaline to litmus. The solution passes through different shades of colour. Care must be taken to make just slightly alkaline. This is done with the help of litmus paper thrown into the solution. Cool. Dilute to about 300 ml.

To the cold solution add from a burette 2 ml. of KI solution and run from a second burette standard silver nitrate solution until a distinct yellow turbidity is obtained. Now run the standard potassium cyanide with constant stirring until the yellow turbidity due to silver iodide is just discharged. In case it is thought that the end-point is considerably passed, the following step is taken to hit off the end-point exactly. Add a few drops more of silver nitrate solution from the burette

until a distinct turbidity is seen. Discharge this by the careful addition of KCN from the burette.

### Standardization of the cyanide solution :—

As potassium cyanide is not available pure, a standard solution of it cannot be made by weighing out a definite quantity and making up the solution in water to an exact volume. The value per ml. of KCN solution in terms of Ni is fixed by putting 1 gm. of a sample of steel of known nickel content through the above process. In the absence of such a standard steel, the following method is adopted wherein the solution of  $\text{AgNO}_3$  is taken as the standard. To the finished assay, add 10 ml. KCN solution, then add  $\text{AgNO}_3$  solution until a turbidity just appears.

### Example and Method of Calculation :—

	KCN	$\text{AgNO}_3$
Sample of steel	28.5 ml.	2.5 ml.
Standardization	10.0 ml.	12.0 ml.

Strength of  $\text{AgNO}_3$  solution is  $\frac{5.8}{17} \times \frac{N}{10}$

Hence strength of KCN solution is  $\frac{12}{10} \times \frac{5.8}{17} \times N/10$

1 litre  $N/10$  KCN =  $\frac{58.7}{2 \times 10}$  gm. Ni.

Volume of KCN solution used for reaction with Ni only

$$= 28.5 - \frac{10}{12} \times 2.5 \text{ ml.}$$

$$= 28.5 - 2.1 \text{ ml.}$$

$$= 26.4 \text{ ml.}$$

26.4 ml. of  $\frac{12 \times 5.8}{10 \times 17} N/10$  KCN =  $\frac{58.7}{2 \times 10} \times$

$$\frac{12 \times 5.8 \times 26.4}{170 \times 1000} \text{ gms. Ni.}$$



$$\begin{aligned}
 1 \text{ gm. steel contains } & \frac{58.7 \times 12 \times 5.8 \times 26.4}{20 \times 170 \times 1000} \text{ gm. Ni.} \\
 100 \text{ gms. contain } & \frac{58.7 \times 12 \times 5.8 \times 26.4 \times 100}{20 \times 170 \times 1000} \text{ gm. „} \\
 \text{Percentage of Ni} & = 3.18
 \end{aligned}$$

NOTES :—

( 1 ) Unlike the indicators used in acidimetry and alkalimetry, there is no quick and sharp indication of the end-point. A certain volume of  $\text{AgNO}_3$  solution is used up to form  $\text{AgI}$  which disappears only after the consumption of a few ml. of  $\text{KCN}$ . This must be determined and allowed for ; otherwise the results for Ni will run high. In the above experiment, 2.1 ml.  $\text{KCN}$  which were used up for reacting with 2.5 ml.  $\text{AgNO}_3$ , have to be deducted from 28.5 ml. before the calculation is made.

( 2 ) From equations ( 1 ) and ( 4 ), it is clear that the atomic weight of Ni divided by 2 will yield a normal solution when present in 1 litre.

( 3 ) The end-point becomes well defined only when Ni is present as  $\text{Ni}(\text{NH}_3)_6\text{SO}_4$ . Hence the addition of  $\text{H}_2\text{SO}_4$  is made.

( 4 ) When more than traces of Cu or Co are present, they must be separated. The former is separated as  $\text{CuS}$  by passing  $\text{H}_2\text{S}$  and the latter by precipitating it with  $\alpha$  nitroso- $\beta$ -naphthol. When Co is present along with nickel, the latter is determined more quickly and easily by means of dimethyl glyoxime.

( 5 ) Chromium, vanadium, tungsten and manganese do not interfere with this method. When the first of these is present, 24 gms. of citric acid will have to be added per gm. of steel

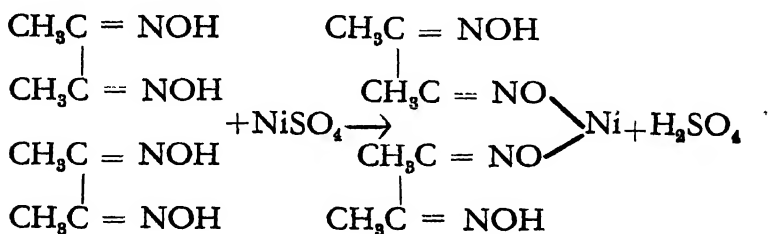
## EXPERIMENT 28.

# Determination of Nickel in Nickel Steel by the Dimethyl Glyoxime Method.

## Principle :—

When a solution of dimethyl glyoxime is added to a faintly alkaline solution of a nickel salt, a voluminous red precipitate appears. This is nickel dimethyl glyoxime. This is filtered off through a Gooch crucible with asbestos felt, washed free of adhering salts, dried in an air oven at 115-120°C. and weighed. From the increase in weight of the crucible the percentage of nickel is calculated.

## The reactions are :



## Solutions required :—

- ( 1 ) Dil. HCl of s.g. 1.1. See Experiment No. 13
- ( 2 ) Dil. HNO<sub>3</sub> of s.g. 1.2 Do.
- ( 3 ) Dil. H<sub>2</sub>SO<sub>4</sub>. Pour 20 ml. conc. H<sub>2</sub>SO<sub>4</sub> into 90 ml. of water in a beaker. Transfer to a bottle.
- ( 4 ) Dilute ammonia s.g. 0.96. See Experiment 11.
- ( 5 ) Dilute acetic acid. Pour 35 ml. of glacial acetic acid into 65 ml. of water in a bottle.
- ( 6 ) 1% dimethylglyoxime solution. Dissolve 1 gm. of dimethylglyoxime in 100 ml. absolute alcohol (ethyl).

1 ml. of this will precipitate 0.002 gm Ni. In the absence of ethyl alcohol, pure methyl alcohol may be used.

### Procedure :—

Dissolve 1 gm. of steel in a 150 ml. beaker in 30 ml. of the dil. hydrochloric acid. Oxidize the ferrous to the ferric condition by adding 20 ml. of the dilute nitric acid. Heat to low bulk, remove from hot plate and add 30 ml. of the dilute sulphuric acid. Transfer to a 600 ml. beaker. Dilute to 400 ml. Add 5-6 gms. tartaric acid, stir until it is dissolved, add dilute ammonia until faintly alkaline ( test with litmus ) and then acetic acid until acid. Raise to a boil and add to the boiling solution 25 ml. of the dimethyl glyoxime solution. Add ammonia until the liquid reacts alkaline or smells slightly of ammonia. Remove from the hot plate. Allow to stand for 10 minutes for the precipitate to settle. Filter through a Gooch crucible which has been dried at  $120^{\circ}\text{C}$ . and has a constant weight. Wash the precipitate with hot water about half a dozen times. Dry in the air oven at  $120^{\circ}\text{C}$ . for an hour. Cool in the desiccator and weigh. Repeat drying to constant weight.

### Example :—

Weight of steel drillings = 1 gm.

Weight of Gooch crucible with the } = 16.9050 gms.  
precipitate

Weight of Gooch crucible alone = 16.760 gms.

Weight of the glyoxime precipitate = 0.159 gm.

1 gm. of sample yields 0.159 gm. of the oxime precipitate  
i.e., 1 gm. sample contains  $0.159 \times 0.2032$  gms. Ni .

100 gms. sample contain  $0.159 \times 0.2032 \times 100$  gms. Ni.

Percentage of Nickel = 3.23

## NOTES :—

(1) This is a very accurate method and in cases of dispute, this method of analysis is adopted.

(2) Copper and cobalt do not interfere.

(3) To prevent the precipitation of Fe as  $\text{Fe}(\text{OH})_3$  when the solution is made alkaline, tartaric acid is added which forms non-ionised iron tartrate and is therefore not precipitated by ammonia. As this acid is somewhat cheaper than citric acid, it is employed.

(4) The precipitate is soluble in mineral acids and in strongly ammoniacal solutions. To neutralize the acid formed when nickel dimethyl glyoxime is precipitated, addition of ammonia is necessary.

(5) In place of ammonia, sodium acetate may be used to react with the mineral acid formed in the course of the precipitation. The acetate must be introduced before the addition of dimethyl glyoxime reagent.

(6) The precipitate of nickel dimethyl glyoxime is soluble in 50% alcohol. Hence, the volume of the solution from which nickel is to be precipitated must be at least 3 or 4 times as large as the volume of the reagent added.

(7) The precipitate of nickel dimethyl glyoxime sublimes at  $250^\circ\text{C}$ . Hence, the heating must be done only at about  $120^\circ\text{C}$ .

(8) When the percentage of nickel is low, the precipitate will have to be allowed to settle for several hours before filtration is commenced.

(9) Tungsten in small amounts does not interfere. When present in large amounts, it must be removed as  $\text{WO}_3$  by repeated evaporation to low bulk, solution in dil.  $\text{HCl}$  and filtration and the determination of nickel then proceeded with.

## EXPERIMENT 29.

\*

**Determination of Nickel in Nickel Steel by Electrolysis.****Principle :—**

When an ammoniacal solution of nickel sulphate or chloride, free from metals which are precipitated by  $\text{H}_2\text{S}$  in acid medium, is electrolysed, nickel is deposited at the cathode. As the iron, separated as  $\text{Fe}(\text{OH})_3$  precipitate, does not interfere, the electrolysis may be carried out in the solution containing the precipitate.

**Procedure :—**

Dissolve 0.3 gm. of the sample in 10 ml. of  $\text{HNO}_3$  of 1.2 s.g. in a tall form beaker of 150-200 ml. capacity. When dissolved, add 20 ml. conc.  $\text{HCl}$ , evaporate to low bulk and repeat two times more, each time adding 20 ml. conc.  $\text{HCl}$ . Neutralize with  $\text{NH}_4\text{OH}$  and then add 20 ml. more of conc.  $\text{NH}_4\text{OH}$ . Add 3 gms. of  $(\text{NH}_4)_2\text{SO}_4$ . Dilute to 150 ml. Electrolyse without filtering off the precipitate of  $\text{Fe}(\text{OH})_3$  and using the current strength shown in the example for the cathode of the area specified. Lift the electrodes from the bath without breaking the circuit, wash with water, break the circuit, and detach the cathode from the binding screw. Wash with alcohol, dry over a spirit lamp flame, cool and weigh. From the increase in weight, calculate the percentage.

**Example :—**

Weight of sample 0.3 gm.

Current strength employed 3.8 amperes.

Temperature of the bath  $25^\circ\text{C}$ .

Duration of the electrolysis—1 hr. 50 minutes.

Area of the cathode surface 30 sq. cms.

Weight of cathode+Nickel deposit=6.4280 gm.

Weight of cathode..... =6.4180 gms.

% of nickel..... =3.33

#### NOTES :

(1) The strength of current required for the given cathode area is drawn from the 220Volt D. C. supply using a lamp-board having several lamps connected in parallel and in series. The diagram of connections and the power of the lamps used is given in Fig. 12.

(2) Due to the presence of  $\text{Fe}(\text{OH})_3$  in the bath, some is likely to be enclosed by the deposit of metal. More accurate results can be obtained by dissolving the deposit in  $\text{HNO}_3$  and repeating the electrolysis in ammoniacal solution, after getting rid of  $\text{HNO}_3$  by repeated evaporation with  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ .

(3) The completion of the deposition is ascertained by repeating the electrolysis for 15 minutes longer. If the cathode does not show any further increase in weight, the deposition is complete.

The values obtained by the three methods for nickel on the same sample of steel are :—

	The Cyanide Method	The dimethyl glyoxime method	The Electrolytic method
Percentage of Nickel	3.23	3.19	3.33

For a full account of the principles of the electro-assay of metals, see Experiment No. 43.

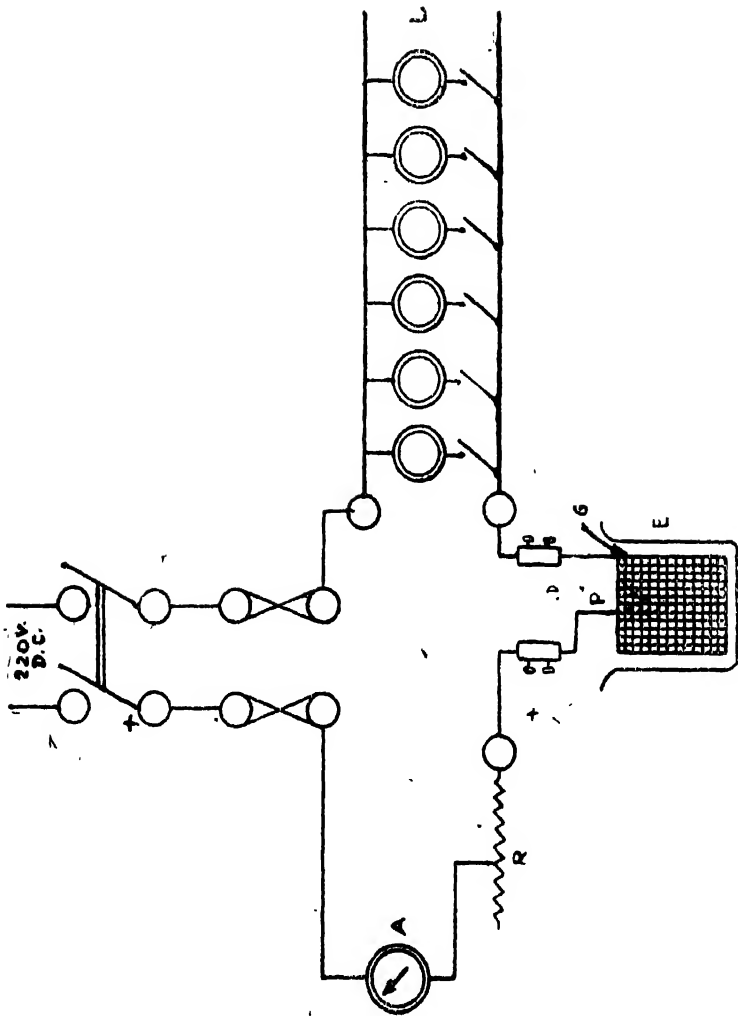


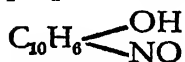
Fig. 12

## EXPERIMENT 30.

**Determination of Cobalt in a Sample of Cobalt Steel.****Principle :—**

When alpha-nitroso beta-naphthol is added to a solution containing Co and Ni, and free from iron, copper, titanium, zirconium, vanadium and nitric acid, both are precipitated as voluminous red compounds. Of these, the precipitate of nickel is soluble in dil. HCl while that of cobalt is insoluble. The precipitate is filtered off through a filter paper, washed free of acid, ignited strongly to  $\text{Co}_3\text{O}_4$  and weighed. From the weight of the oxide, the percentage of Co is calculated.

**Reagent :—**Dissolve 1 gm. of  $\alpha$ -nitroso  $\beta$ -naphthol in 15 ml. of glacial acetic acid. The reagent should be prepared fresh each time it is required. Its formula is

**Procedure :—**

Dissolve 2 gms. of the drillings in a 400 ml. beaker with 50 ml. of 1.16 s.g. HCl on the hot plate. Add 10 ml.  $\text{HNO}_3$  ( s.g. 1.2 ) and evaporate until the salts begin to separate. Boil with water, transfer to a 500 ml. measuring flask, add an emulsion of zinc oxide and shake well. Continue the addition of zinc oxide until the supernatant layer is milky. Cool to room temperature and dilute to the mark. Mix thoroughly and allow to settle. Filter through a dry filter-paper into a clean, dry 250 ml. measuring flask. Reject the first few ml. of the filtrate. When the filtrate reaches the 250 ml. mark, pipette off 25 ml. into a tall 400 ml. beaker. Add 7 ml. of conc. HCl and 100 ml. of water. Heat to boiling, add 5 ml. of a solution of  $\alpha$  nitroso  $\beta$ -naphthol. Stir well. Allow to settle in a warm place for about



2 hrs. Filter hot and wash with dil. HCl ( 1:2 ) which is at about  $80^{\circ}\text{C}$ . until the washings show no test for Ni. ( Use the dimethyl glyoxime reagent for the purpose. Make the filtrate to be tested slightly alkaline with ammonia and add a few drops of the reagent. Absence of red colour shows nickel has been removed by washing ). Wash free of HCl with hot water. 10-12 washings will be necessary. Dry, slowly char the paper with the precipitate in a porcelain or a platinum crucible without allowing the filter paper to take fire and then ignite in a muffle furnace having a temperature of  $1000^{\circ}\text{C}$ . for half an hour. Cool and weigh.

#### NOTES—

( 1 ) The elements that interfere with the method are iron, chromium and copper. The removal of the two first ( Fe and Cr ) is effected by zinc oxide, which brings them down as the respective hydroxides. Copper, when present, must be first removed by means of  $\text{H}_2\text{S}$ . The filtrate from the copper sulphide is freed from  $\text{H}_2\text{S}$ , the iron oxidized to the ferric state and then the precipitation by means of zinc oxide proceeded with. When the percentage of cobalt is about 3-4, it is necessary to re-dissolve the ferric hydroxide in dil HCl, repeat separation of cobalt by treatment with zinc oxide, add the filtrate obtained to the original filtrate and proceed for the cobalt determination with the combined filtrate. The other interfering elements are titanium and vanadium. For the method of testing for the presence of these, see Chapter XI.

( 2 ) As the cobalt precipitate is very voluminous, small amounts of cobalt only must be used for the precipitation.

( 3 ) The determination of nickel may be made on the filtrate by evaporating it to dryness with conc.

$\text{HNO}_3$  and fuming with conc.  $\text{H}_2\text{SO}_4$  and then proceeding as described under the determination of nickel by the dimethyl glyoxime method.

( 4 ) The compound precipitated has the formula  $(\text{C}_{10}\text{H}_6\text{ONO})_3\text{Co}$ .

( 5 ) This method serves for the determination of cobalt present in small quantities in nickel steel and also for the determination of large amounts, 3-5%, intentionally introduced in high speed steels.

( 6 ) The reagent will precipitate nickel also, if the solution to which it is added does not contain 5%  $\text{HCl}$ . For every 100 ml. of solution from which cobalt is precipitated, there should be 5 ml. conc.  $\text{HCl}$  to prevent nickel being precipitated.

( 7 ) The method is accurate only when the ignited precipitate weighs a few milligrams. For residues weighing more, it is necessary to adopt the electrolytic method. This need arises from the fact that the ignited residue is of uncertain composition.

The solution for electrolysis is obtained as follows:—

The precipitate of cobalt nitroso- $\beta$ -naphthol, washed free of the precipitant and acid, is transferred to the beaker in which the precipitation was made, 20 ml. concentrated nitric acid added and the contents of the beaker boiled to destroy the organic matter. 5 ml. concentrated sulphuric acid are then added and the boiling continued until copious fumes of sulphur trioxide are evolved. The solution is cooled and diluted to about 100 ml. The solution is made strongly ammoniacal and 3 gms. of ammonium sulphate added. From this point the details are the same as those for the determination of Ni shown in Experiment No. 29.

## EXPERIMENT 31.

**Determination of Chromium, Vanadium and Tungsten in a Sample of High Speed Steel.****( Without a Preliminary Separation of Iron )**

**Principle :—** On dissolving the sample of steel in conc. HCl followed by the addition of conc.  $\text{HNO}_3$ , tungsten separates as  $\text{WO}_3$ , chromium remains in solution as  $\text{CrCl}_3$  and vanadium as vanadyl chloride of the formula  $\text{VOCl}_2$ . The residue of  $\text{WO}_3$  is filtered off through pulp filter, ignited, weighed and purified. The filtrate containing the chromium and the vanadium is evaporated to fumes with conc.  $\text{H}_2\text{SO}_4$ , the residues dissolved in water and oxidized by a solution of  $\text{KMnO}_4$  to  $\text{H}_2\text{CrO}_4$  and  $\text{HVO}_4$ . These are determined by titrating with standard solutions of  $\text{FeSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $6\text{H}_4\text{O}$  and  $\text{KMnO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ .

**Reagents required :—**

1. Conc. HCl.
2. Conc.  $\text{HNO}_3$ .
3. Conc.  $\text{H}_2\text{SO}_4$ .
4. 4%  $\text{KMnO}_4$  solution.
5.  $\text{MnSO}_4$ .

With a view to economise time and material all the determinations are made from one weighing of the sample only.

**Procedure :—**

Weigh 0.5 gm. sample into a 200 ml. casserole or dish. Add 25 ml. conc. HCl and heat nearly to boiling. Add from time to time a few drops of conc.  $\text{HNO}_3$  from a dropping bottle until the steel is completely dissolved. When decomposition of the steel is complete without the separation of a yellow residue of  $\text{WO}_3$ , add

5 ml. more of conc.  $\text{HNO}_3$ , evaporate to dryness, dissolve the residue by heating with 30 ml. of 1.1  $\text{HCl}$ , add 25ml. water and boil for a few minutes longer. Filter through a pulp filter. Pulp is prepared by shaking two or three ashless filter papers of 11 cm. diameter, torn into very small bits, with 40–50 ml. of distilled water in a corked Erlenmeyer flask of 250–300 ml. capacity until the papers are well macerated. Pour the pulp so obtained after the addition of 100 ml. more of water on to a 11 cm. filter paper fitted to a funnel passing through a cork in a filter flask. Alternatively, place in a horizontal position a filter-disc of glass or porcelain in a funnel, close the bottom of the stem with the finger, pour water until the stem is full and the disc is covered. Then add pulp, allow the water to run out, press pad with flattened glassrod and proceed. Wash with 1 : 10  $\text{HCl}$  until free from iron, using suction. Reserve filtrate for the determination of chromium and vanadium. Dry the filter paper, transfer to a platinum crucible and ignite at a dull red heat. Cool in a desiccator and weigh. The ignited residue consists of the following:— $\text{WO}_3$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ .....(A). To free the residue from  $\text{SiO}_2$ , moisten it with a few drops of 1 : 3  $\text{H}_2\text{SO}_4$ , add about 5 ml. of  $\text{HF}$  and heat on the hot plate in a fume chamber with a good draught. When dry, expel the  $\text{H}_2\text{SO}_4$  by heating the crucible to a dull red *at the top*. When no more  $\text{SO}_3$  fumes escape, cool and weigh. This weighing represents the weight of the following — $\text{WO}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Cr}_2\text{O}_3$ . (B). To obtain the weight of  $\text{WO}_3$ , proceed as follows:—Add 3–4 gms of pure  $\text{Na}_2\text{CO}_3$  and a few milligrams of tartaric acid to the residue in the crucible and fuse either over a Bunsen burner or at the mouth of a muffle furnace until the  $\text{WO}_3$  is completely dissolved. Cool. Remove cake from the crucible

by light pressure—by rotating between the palms. Digest it with 100 ml of water in a porcelain basin until no hard lumps remain. Filter through 7 cm. paper. Wash until the washings are free from alkali. Test with phenolphthalein. Ignite the paper with the residue in a platinum crucible and weigh. This weight 'C' yields the amount of  $\text{Fe}_2\text{O}_3 + \text{Cr}_2\text{O}_3$  present in (B). 'C' subtracted from 'B' yields the weight of  $\text{WO}_3$  from which the % of W is calculated.

NOTES:—

(1) A 5 to 10 gm. sample will be required for determining small percentages of tungsten. If tungstic acid separates before the decomposition of the steel is complete, not only is the acid thus separating contaminated with too large an amount of  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  but the decomposition of the steel itself is incomplete and therefore correct results for tungsten cannot be obtained. Hence the addition of conc.  $\text{HNO}_3$  must be gradual and must be made in small quantities only at a time until the steel is completely decomposed.

(2) The object of evaporation to dryness is to dehydrate the silicic acid which is also formed along with the tungstic acid.

(3) Filtration through pulp using suction is rapid and the tendency of the tungstic acid to creep to the edges of the filter paper is entirely prevented thereby.

(4) The evaporating basin or casserole used has a ring of yellow which is removed as follows:—Drop pieces of filter paper moistened with  $\text{NH}_4\text{OH}$  on to the dish when it has been thoroughly washed. Wipe the yellow stain due to tungstic acid with the paper. Add these pieces to the main precipitate of  $\text{WO}_3$  in the

crucible.  $\text{WO}_3$  is an acid readily dissolving in ammonia. On ignition  $\text{NH}_3$  escapes leaving behind  $\text{WO}_3$ .

(5) Ignition of  $\text{WO}_3$  residues at temperatures above  $800^\circ\text{C}$ . leads to loss, as  $\text{WO}_3$  begins to volatilize at temperatures higher than this.

(6) The addition of a few milligrams of tartaric acid to  $\text{Na}_2\text{CO}_3$  provides a reducing atmosphere, preventing the formation of  $\text{Na}_2\text{CrO}_4$ . If the tartaric acid were to be omitted, some  $\text{Na}_2\text{CrO}_4$  will be formed and the amount of Cr will have to be determined from the filtrate either by titration with  $0.05\text{ N FeSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $6\text{H}_2\text{O}$  or by colorimetry. Both the operations will consume time. The reducing fusion recommended above obviates the necessity for such a step, as all the Cr, present as  $\text{Cr}_2\text{O}_3$  originally, remains in the same condition after fusion and is therefore easily allowed for. Tartaric acid decomposes on heating into  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{C}$ . These furnish a reducing atmosphere.

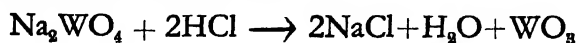
(7) Where very great accuracy is needed, the filtrate must be evaporated to dryness a second time, redissolved in  $1 : 1\text{ HCl}$ , boiled and filtered through a separate filter paper with pulp. The two residues are then dried and ignited as described above. This procedure becomes necessary on account of the fact that both  $\text{WO}_3$  and  $\text{SiO}_2$  remain in solution to a slight extent after a single evaporation. The slight amount must be recovered by filtering off the major portion of the acids which separate after a single evaporation to dryness, evaporating the filtrate again to dryness and again redissolving and filtering through a second paper. Repeated evaporations alone without removing the major portion of the acids namely,  $\text{WO}_3$  and  $\text{SiO}_2$ , by filtration are of no use.

(8) Both W and Si form volatile fluorides. To retain W, it is necessary to add a few drops of  $\text{H}_2\text{SO}_4$  previous to the addition of HF.

(9) If molybdenum is present in the sample of steel, some of it will contaminate  $\text{WO}_3$ . The amount contaminating it is determined from the filtrate obtained by filtering off the extract of the fusion with  $\text{Na}_2\text{CO}_3$  and  $\text{H}_3\text{C}_4\text{O}_6$ .

(10) When only tungsten is to be determined, the second evaporation to dryness may be dispensed with and the following procedure adopted:-- Add to the filtrate 1 gm. of cinchonine hydrochloride dissolved in 10 ml. of 1:1 HCl or 0.5 gm. of the base (cinchonine) dissolved in 20 ml. of 1:1 HCl. Heat for half an hour at about  $95^\circ\text{C}$ . and filter. Wash with a very dilute solution of cinchonine hydrochloride (1 gm. of substance in 990 ml. of water and 10 ml. of 1 : 1 HCl) until free from iron. Ignite. Cool and weigh as tungstic acid ( $\text{WO}_3$ ). Add the weight obtained to that obtained by igniting the main residue i. e., to 'B minus C'.

(11) When sodium tungstate solution is evaporated to dryness with HCl the following reaction does not proceed to completion :—



The tungstic acid that separates is contaminated with sodium meta tungstate and the tungsten cannot therefore be accurately determined by igniting the residue and weighing it. But if a solution of cinchonine hydrochloride is added to the acidified solution of sodium tungstate and the mixture heated to boiling, the tungstic acid separates in a pure condition. This can be filtered off, ignited and weighed. Cinchonine hydro-

chloride has the formula  $C_{19}H_{22}ON_2 \cdot HCl \cdot 2H_2O$ . Its solubility is 4.5 gms. per 100 ml. of water at room temperature.

### Determination of Chromium and Vanadium from the Filtrate:—

**Procedure :—** Evaporate the filtrate from the impure tungstic acid in a casserole with 6 ml. conc.  $H_2SO_4$  to dense white fumes. Cool. Cautiously dilute with water to about 150 ml. Boil and transfer to a 600 ml. beaker. Add 4%  $KMnO_4$  solution from a pipette drop by drop until the liquid is pink decidedly and continues to be so on 5 minutes' boiling. Add a few milligrams at a time of  $MnSO_4$  until the pink colour is destroyed and only a brown precipitate remains. Cool. Filter through a Gooch crucible with asbestos-layer and wash 10 times with hot water. Transfer the filtrate to a 600 ml. beaker. Cool to room temperature. To the cold filtrate add 20 ml. of normal sulphuric acid and run from a burette standard ferrous ammonium sulphate until the liquid is green and then 10-20 ml. in excess. Test for excess on the spot plate with a solution of potassium ferricyanide, (0.1 gm. of the salt in 50 ml. water). Run from a burette standard  $KMnO_4$  until the liquid is pink and remains so for a minute. If  $KMnO_4$  and  $FeSO_4$ ,  $(NH_4)_2SO_4$ ,  $6H_2O$  solutions are exactly 0.05 N, then the number of ml. of the former subtracted from that of the latter is a measure of the amount of chromium in the sample. To determine the vanadium which is, at this stage, present in the solution as vanadic acid, proceed as follows :—

Add 20-25 ml of the same standard ferrous ammonium sulphate solution, as was used for the determination of chromium, to the beaker. Test for the presence of excess with a solution of potassium ferricyanide,



Use the spot plate. Titrate excess with 0.1 N  $K_2Cr_2O_7$ . The following example will make clear the process of calculation for chromium and vanadium :—

Weight of steel taken 0.5 gm.

Volume of 0.05 N  $FeSO_4$  used : Burette Reading :—

Final 50.0 }  
Initial 0.0 } 50.0 ml.

Volume of 0.05 N  $KMnO_4$  used :

Final 31.0 }  
Initial 0.0 } 31.0 ml.

Volume of 0.05 N  $FeSO_4$  used to react with }  
the chromic acid formed from Cr in the steel. } 19.0 ml.

1 litre of 0.05 N  $FeSO_4$  is equal to 1 litre of 0.05 N  $H_2CrO_4$  (i.e.)  $\frac{2 \times 52}{6 \times 20}$  gms. of chromium.

Therefore 19 ml. 0.05 N  $FeSO_4 = \frac{2 \times 52 \times 19}{6 \times 20 \times 1000}$  gms. Cr

0.5 gm. steel sample contains  $\frac{2 \times 52 \times 19}{6 \times 20 \times 1000}$  gms. Cr

100 gms. , ,  $\frac{2 \times 52 \times 19 \times 200}{6 \times 20 \times 1000}$  gms. Cr

that is.....3.28% Cr.

The determination of vanadium is proceeded with, using the titrated solution, V being present in it as  $H_2VO_4$ . Make up the solution to 500 ml. in a measuring flask. Divide into two parts. Titrate one part.

Volume of 0.05 N  $FeSO_4$ —Burette readings :

Final 12.4

Initial 1.5

---

10.9 ml.

Volume of  $K_2Cr_2O_7$  used—Burette readings Final. .19,9

Initial. .10.0

---

9.9ml.

### Titration values to find the strength of $K_2Cr_2O_7$

$0.05\text{ N FeSO}_4$	$\text{K}_2\text{Cr}_2\text{O}_7$
<u>14.8 ml</u>	<u>15.0 ml.</u>

Hence 15 ml. of  $K_2Cr_2O_7$  = 14.8 ml. 0.05 N  $FeSO_4$   
 9.9 ml                   ,,       =  $14.8 \times 9.9 / 15.0$  ml.  
                                       = 9.8 ml.

Amount of 0.05 N  $\text{FeSO}_4$  added = 10.9 ml.

Excess found = 9.8 ml.

Therefore, volume of 0.05 *N* FeSO<sub>4</sub> used to reduce vanadic acid = 1.1 ml.

$$\begin{aligned} 1 \text{ litre } 0.05 \text{ N } \text{FeSO}_4 &= 1 \text{ litre } 0.05 \text{ N } \text{V}_2\text{O}_5 \\ &= 51/20 \text{ gms. V.} \end{aligned}$$

$$1.1 \text{ ml. } 0.05 \text{ N FeSO}_4 = \frac{51 \times 1.1}{20 \times 1000} \text{ gm V.}$$

0.25 gm. steel contains                   "       "       "

100 gms. „  $51 \times 1.1 \times 4 \times 100 / 20 \times 100$  gm. V.  
that is „ 1.12% V.

Alternatively, the following procedure may be adopted for the determination of vanadium :—

Make up the solution, left after the determination of chromium is finished, to 500 ml. in a measuring flask. To 250 ml. of the solution add with constant stirring approximately 0.1 N ferrous sulphate solution from a burette until it is present in excess. This is indicated by testing with the external indicator, potassium ferricyanide. Add 3-5 ml. in excess. Add about 10 ml. of a freshly prepared 10% solution of ammonium persulphate and stir vigorously. Add 0.03 N potassium permanganate solution from a burette until a pink colour persisting for about a minute is obtained.

$$1 \text{ ml. } 0.03 \text{ N KMnO}_4 = 0.00153 \text{ gm. V.}$$

The principle of the above is based on the fact that

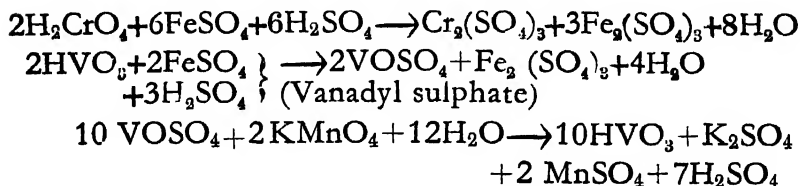
in cold solutions, ammonium persulphate is without effect on chromium, i. e., it does not oxidize it from the trivalent to the hexavalent state. Nor does it oxidize vanadium from the tetra to the pentavalent state. It, however, oxidizes the ferrous to the ferric state.

The above procedure can be adopted only after the elimination of tungstic acid in the manner described.

The end-point obtained may be made more sharp by the addition of about 5–10 ml. of phosphoric acid which suppresses the colour due to ferric salts.

This method of determination of vanadium has been introduced in recent years and is very rapid.

The reactions involved in the determination of chromium and vanadium may be expressed as follows:—



#### NOTES :—

(1) The oxidation of vanadium from the tetravalent to the pentavalent state by potassium permanganate takes place very readily at 70°C. At room temperature, the oxidation is slow. Hence the permanganate solution should be added with constant stirring and the end point should be taken as reached only when the pink colour does not fade within a minute after the same is apparently reached.

(2) When there is any difficulty experienced in bringing the steel into solution in hydrochloric and nitric acids as described, dilute sulphuric acid 1:3 should be used along with orthophosphoric acid. Add at the rate of 5 ml. per gm. steel.

(3) A blank should be run to allow for the number of drops of standard permanganate required to impart a color of the same intensity as in the run. The chromium sulphate solution is green and to obtain an easily discernible pink color indicating the completion of oxidation of vanadium, it would require a few drops of the standard solution of potassium permanganate. In view of the small percentages of vanadium ordinarily present in steel, and in view of the need for an accurate determination of the same, it is necessary to ascertain this blank and allow for it.

**Procedure :—**

Boil the solution which is left after determining vanadium, for about 10 minutes. This decomposes the excess permanganate. Cool to room temp. Now add the same standard permanganate solution until a pink color of the same intensity as in the actual run is obtained. Subtract the number of ml. from the volume already added and then calculate the vanadium content.

## EXPERIMENT 32.

### **Determination of Vanadium in Steel (Alternative Method based on a preliminary separation of Iron and Chromium. )**

**Principle :—**

When the sample is dissolved in a mixture of HCl and  $\text{HNO}_3$ , the vanadium passes into solution as vanadyl chloride. The other metals present in the steel are changed to chlorides. The latter are precipitated as hydroxides, while the former remains in solution as sodium hypovanadate, when the solution of the steel is poured into sodium hydroxide solution. The

precipitated hydroxides are filtered off. The filtrate containing V as sodium hypovanadate ( $\text{Na}_4\text{V}_2\text{O}_6$ ) is neutralized with HCl, oxidized and treated with  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  when a precipitate of basic vanadate of lead approximating in composition to the formula,  $2\text{Pb}_2\text{V}_2\text{O}_7$ ,  $\text{PbO}$ , is obtained. This is filtered off and ignited. The ignited residue, on treatment with  $\text{H}_2\text{SO}_4$ , yields  $\text{PbSO}_4$  which is filtered off. The filtrate contains the V as  $\text{H}_3\text{VO}_4$ . This is reduced to  $\text{V}_2\text{O}_3(\text{SO}_4)_2$  by  $\text{SO}_2$ , the excess  $\text{SO}_2$  expelled by boiling, and the  $\text{V}_2\text{O}_3(\text{SO}_4)_2$  oxidized to  $\text{H}_3\text{VO}_4$  by standard  $\text{KMnO}_4$ . The number of ml. of std.  $\text{KMnO}_4$  measures the amount of V in the sample.

#### **Procedure :—**

Dissolve 1 gm. of the sample in HCl and  $\text{HNO}_3$  exactly as described under 'Procedure' in Expt. 31. Filter off the tungstic oxide. Evaporate the filtrate to about 15-20 ml. Treat with 10% NaOH solution until the excess acid is neutralized. Test with litmus paper. Transfer the neutralized solution to a tap-funnel. Run this solution a little at a time, into a dish containing 10 gms. NaOH dissolved in 100 ml. water. Stir well while adding. Wash the tap-funnel two or three times with water. Run the washings into the dish. Filter off the hydroxides of Fe, Cr, Ni, and Mn. Wash the precipitate and paper two or three times with water.

Dissolve the precipitate of hydroxides on the filter paper in HCl. Repeat the above process of running the solution into NaOH solution. Filter. Add a few drops of methyl orange and neutralize by the careful addition of dil. HCl. Add drop by drop 0.2 N- $\text{KMnO}_4$  until the pink color fades very slowly. Add 20 ml. of 4% lead acetate solution and 20 ml. of 35% ammonium acetate solution. Boil and digest on the hot plate for half an hour.

Filter off the precipitate of basic pyro-vanadate of lead through paper pulp (see Expt. 31), wash with water, dry and ignite at a low temperature in a porcelain crucible until the paper with pulp is ashed.

Treat the cold ignited residue in a beaker with 10 ml. conc. HCl and a few drops of conc.  $\text{HNO}_3$ . Boil until dissolved. Add 5 ml. conc.  $\text{H}_2\text{SO}_4$  and evaporate to strong fumes in a Pyrex glass beaker. Cool. Pour into 50 ml. of water in a second beaker. Rinse the original beaker well with water and transfer the rinsing to the second beaker. Filter off the lead sulphate. Collect the filtrate in a 300 ml. Erlenmeyer flask. Add 5 ml. of sulphurous acid solution. Boil until the excess of  $\text{SO}_2$  is expelled. Test by passing the gases evolved into acidified  $\text{KMnO}_4$  of 0.01 N strength. For this purpose, fit the Erlenmeyer flask with a two-holed cork carrying glass-tubing bent at right angles.  $\text{CO}_2$  is bubbled through the solution by means of one of the tubes. The exit gases pass through the other.

Take 2-5 ml. of dil.  $\text{H}_2\text{SO}_4$  (1 : 10) in a test tube. Add a drop of 0.01 N  $\text{KMnO}_4$  to it. Pass the steam evolved in the Erlenmeyer flask into the solution. If the pink color does not disappear in the test tube, the solution in the flask is free from  $\text{SO}_2$ . Titrate when at about  $70^\circ\text{C}$ . with 0.01 normal  $\text{KMnO}_4$ .

### Example and Calculation :—

Weight of sample taken = 1 gm.

Volume of 0.01 N- $\text{KMnO}_4$  required = 20.7 ml.

∴ 1 ml. 0.01 N- $\text{KMnO}_4$  = 1 ml. 0.01 normal  $\text{V}_2\text{O}_5$

$$= \frac{51}{100} \times \frac{1}{1000} \text{ gm. V}$$

$$20.7 \text{ ml. } 0.01 \text{ N-}\text{KMnO}_4 = \frac{51 \times 20.7}{100 \times 1000} \text{ gm. V}$$

$$\begin{aligned}\text{Percentage of vanadium} &= \frac{51 \times 20.7 \times 100}{100 \times 1000} \\ &= 1.055\end{aligned}$$

**NOTES :—**

(1) The separation of vanadium from Fe, Cr, Ni and Mn is complete only when the solution of steel is run into alkali hydroxide solution. If the alkali solution is added to the solution of the steel sample, a precipitate of basic ferric hypo-vanadate will be formed, which it is difficult to decompose by excess of NaOH solution added subsequently.

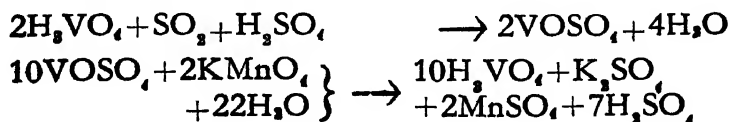
(2) Double precipitation of Fe, Ni, Cr, and Mn is necessary to recover the V which is occluded by the hydroxide precipitates.

(3) The addition of a few drops of  $\text{KMnO}_4$  is to oxidize vanadyl chloride to vanadic acid, the precipitation of V by lead acetate being complete only when it is present as vanadic acid.

(4) Ammonium acetate prevents the formation of insoluble lead chloride along with pyrovanadate of lead.

(5) On evaporation to fumes with  $\text{H}_2\text{SO}_4$ , the ignited pyrovanadate of lead yields  $\text{H}_3\text{VO}_4$ , which is soluble and  $\text{PbSO}_4$ , which is insoluble. The sulphate is filtered off.

(6) The reactions which take place when  $\text{H}_3\text{VO}_4$  is reduced with  $\text{SO}_2$  and  $\text{KMnO}_4$  oxidizes the reduced solution, are as follows :—



(7) The composition of the precipitate of basic ~~metavanadate~~ of lead depends on the conditions. As ~~an hour~~ is difficult to control to a nicety, the precipitate

is of varying composition. Hence it is not possible to get the percentage of V by igniting the same and weighing it.

(8) Molybdenum when present in small quantities does not interfere with the method. On the addition of lead acetate it is precipitated as lead molybdate. When this is heated to fumes with  $\text{H}_2\text{SO}_4$ ,  $\text{MoO}_3$  is obtained. The reduction in strongly acid solution of small amounts of  $\text{MoO}_3$  by  $\text{SO}_2$  does not take place. When Mo is present in large amounts and the solution is slightly acid, its reduction, however, will take place and the results for V will run high. In that case proceed as follows :—

To the mixture of  $\text{H}_3\text{VO}_4$  and  $\text{H}_2\text{MoO}_4$  add ammonia until alkaline. Suppose the volume of the solution is 50 ml. Add 1 gm. tartaric acid. Shake until dissolved. Add 2 ml. concentrated  $\text{H}_2\text{SO}_4$ . Pass  $\text{H}_2\text{S}$  for 10 minutes. Filter off the molybdenum sulphide. Pass  $\text{H}_2\text{S}$  into the filtrate to test for the completeness of precipitation. Evaporate the filtrate to fumes with conc. sulphuric acid. This process destroys tartaric acid. Dilute with water. Add 4%  $\text{KMnO}_4$  solution until pink. Reduce with  $\text{SO}_2$ . Boil off the excess  $\text{SO}_2$ , pass a current of  $\text{CO}_2$  to drive out the last traces of  $\text{SO}_2$ . Titrate with 0.03 N  $\text{KMnO}_4$ . Tartaric acid addition prevents the precipitation of vanadium as sulphide along with molybdenum.

### EXPERIMENT 33.

#### **Determination of Molybdenum in Steel. ( Absence of Vanadium and Tungsten. )**

**Principle :—**

When the steel sample is dissolved in a mixture of  $\text{HCl}$  and  $\text{KClO}_3$ ,  $\text{MoCl}_6$  ( molybdenum hexachloride )



is formed. By pouring the solution of steel containing this into sodium hydroxide solution, sodium molybdate is formed and the iron is thrown down as  $\text{Fe}(\text{OH})_3$ . This is filtered off. The filtrate is acidified with  $\text{HCl}$  and the molybdic acid is precipitated as  $\text{PbMoO}_4$  by the addition of  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  and  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ . The precipitate is allowed to settle, filtered off through pulp filter, dried, ignited and weighed. From the weights of steel taken and  $\text{PbMoO}_4$  obtained, the percentage of molybdenum is calculated.

### Solutions required :—

( 1 ) Approximately 2 N NaOH solution. Dissolve 20 gm. NaOH in 250 ml. water.

( 2 ) Lead acetate solution. Dissolve 1 gm. lead acetate in 25 ml. water.

( 3 ) Ammonium acetate solution. Dissolve 8 gms of the salt in 25 ml. water.

### Procedure :—

Dissolve 2 gms. of the steel in a 250 ml. beaker in 20 ml. conc. hydrochloric acid. Add 1 gm.  $\text{KClO}_3$ . Dilute to 100 ml. with water. Boil until all the chlorine gas is expelled. Add solution No. 1 until most of the free acid is neutralized. There should not appear any precipitate. Transfer the solution to a tap-funnel. Take 150 ml. of solution No. 1 in a 500 ml. beaker and heat to boiling. Run from the tap-funnel the iron solution into the hot caustic soda solution, keeping the latter stirred during the addition. Rinse the tap-funnel twice with 10 ml. water. Run the rinsings into the caustic soda solution. Make up to 500 ml. with water. Note the temperature of the contents of the 500 ml. flask. Filter hot through a 15 cm. dry filter paper. Collect the filtrate in a 250 ml. measuring flask. When a little

above the mark, note the temperature of the filtrate. Bring it to the one noted in the case of the contents of the 500 ml. flask by keeping it in a hot water bath. When of the correct temperature, draw off the liquid above the mark by a pipette and throw away. Transfer the contents of the 250 ml. flask to a 600 ml. beaker. Neutralize with concentrated hydrochloric acid. Add 1 to 2 ml. in excess. Boil. Add 15 ml. of solution No.2 and 20 ml. of solution No. 3. Heat to boiling. Let stand for about 20 minutes and then filter through pulp. Wash free of chloride. Transfer filter paper with residue to a porcelain crucible. Dry at the mouth of a muffle furnace. Push gradually into the interior when dry. When perfectly white, cool in a desiccator and weigh.

#### Results and Calculation :—

Weight of steel	= 2 gms.
Wt. of steel from which Mo was precipitated	= 1 gm.
Wt. of crucible + $\text{PbMoO}_4$	= 12.4368 gms.
Wt. of crucible	= 12.4066 gms.
Wt. of $\text{PbMoO}_4$	= 0.0302 gms.
Mo%	= 0.85

#### Procedure when Tungsten and Vanadium are present :—

The method described above requires modification when tungsten and vanadium are also present in the steel. After solution in  $\text{HCl}$  and  $\text{HNO}_3$ , the former is separated as  $\text{WO}_3$  by two evaporations to very low bulk. The separated tungstic acid is removed, after the addition of 30 ml. conc. hydrochloric acid, followed by 20 ml. water, by filtration. Vanadium is not eliminated by this means. It accompanies the molybdenum and is precipitated along with the latter as a basic

vanadate of lead. The precipitate is ignited and when cold treated with conc. sulphuric acid. Lead is thrown down as  $\text{PbSO}_4$ . After dilution and settling, this is filtered off. The filtrate contains the molybdenum and the vanadium as molybdic and vanadic acids.

### **Principle of Separation of $\text{V}_2\text{O}_5$ from $\text{MoO}_3$ :—**

When into a hot solution of the mixed acids containing 5% sulphuric acid by volume (5 ml. conc.  $\text{H}_2\text{SO}_4$  for every 100 ml. of soln.) hydrogen sulphide is passed,  $\text{MoS}_3$  separates as a brown precipitate, the V remaining in solution. The precipitate is filtered off through a Gooch crucible packed with asbestos, ignited until  $\text{SO}_2$  ceases to come off, cooled and weighed as  $\text{MoO}_3$ .

### **Procedure :—**

Neutralize the filtrate from  $\text{WO}_3$  containing  $\text{MoO}_3$  and  $\text{V}_2\text{O}_5$  by means of ammonia until faintly smelling of it. Add 20 ml of  $2\frac{1}{2}\%$  sulphuric acid (1 ml. conc. sulphuric acid in 50 ml. water). Dilute to 200 ml. Heat to boiling. Pass hydrogen sulphide until cold. Filter through a Gooch crucible. Wash with  $2\frac{1}{2}\%$  sulphuric acid saturated with hydrogen sulphide. Ignite and weigh. From the weight of  $\text{MoO}_3$ , calculate the percentage of molybdenum.

The ignition of molybdenum trisulphide to oxide is best carried out in an electric muffle furnace whose temperature can be very carefully controlled. It must be measured by means of a pyrometer and must not exceed  $525^\circ\text{C}$ . Above this temperature, molybdenum trioxide is appreciably volatilized.

When molybdenum is present in small amounts, the following colorimetric method is adopted :—

### **Principle of the Method :—**

When to a solution containing molybdenum in the

quinuevalent stage, a solution of potassium thiocyanate is added, a brown or red color is formed, depending upon the amount of molybdenum present. As the procedure for dissolving the sample yields molybdic acid in which molybdenum is hexavalent, it is necessary to add a reducing agent which will reduce molybdenum to the quinuevalent stage. The reducing agent employed is a solution of stannous chloride. In this method, the ferric chloride present is also reduced by the stannous chloride solution to colorless ferrous chloride and there is therefore no masking of the colour due to the molybdenum compound.

The masking of the colour, however, due to the presence of chromium, if any, must be allowed for by adding to the standard solution of molybdenum a like amount of chromium in the form of chromium sulphate.

The intensity of colour is influenced by temperature, acidity of the medium, and the amount of stannous chloride. It is therefore necessary to maintain them the same in both the standard and the sample. The colour tends to fade on standing. Therefore the comparison should be made immediately after the addition of potassium thiocyanate solution.

### **Solutions required :—**

- (1) Nitric-Sulphuric Acid for solution of the sample.
 

Nitric acid S.G. 1.20	..	833 ml.
Sulphuric acid ( 1:1 )	..	167 ml.
- (2) Sulphuric-Hydrochloric acid, the medium in which the color comparison is made.
 

Sulphuric acid ( 1:1 )	..	450 ml.
Hydrochloric acid ( s.g. 1.12 )	..	100 ml.
Water	..	150 ml.

- (3) Ferric sulphate solution for mixing with the standard sodium molybdate solution.

Ferric sulphate	..	70 gms.
Hydrochloric acid ( 1:1 )	..	120 ml.
Sulphuric acid ( 1:1 )	..	500 ml.
Water	..	380 ml.

- (4) Chromium sulphate solution.

50 gms. of chrome alum are dissolved in 100 ml. of sulphuric acid ( 1:1 ) and 200 ml. of water and the solution is heated until the purple color changes to green. The solution is then diluted to 1000 ml.

- (5) Stannous chloride solution.

Stannous chloride ( $\text{SnCl}_2, 2\text{H}_2\text{O}$ )	...	350 gm.
Hydrochloric acid ( 1:1 )	...	200 ml.
Water freshly boiled and cooled to make		1000 ml.
Metallic tin		2-3 gms.

The stannous chloride is weighed into a 500 ml. conical flask, the dilute acid added and the mixture is boiled gently until the salt is in solution. The warm solution is transferred to a glass-stoppered bottle of 1 litre capacity which contains the boiled and cooled water. Tin is added in small pieces and the bottle kept stoppered. Note that this solution is much stronger than the solution used in Experiment 10.

- (6) Standard Sodium Molybdate solution.

Sodium molybdate ( $\text{Na}_2\text{MoO}_4, 2\text{H}_2\text{O}$ )		1.2604 gm.
Sulphuric acid (1:1)	..	10 ml.
Water	..	990 ml.

Introduce about 600 ml. water into 1 litre measuring flask and 10 ml. of the sulphuric acid. Dissolve the weighed amount of molybdate in the measuring flask. When dissolved make up to the mark and mix thoroughly. 1 ml. of this solution = 0.0016 gm. molybdenum.

The value of the standard in terms of molybdenum should be ascertained by putting 100 ml. of the solution through the Jones Reductor described in the next experiment, i.e., Experiment 34.

(7) Potassium thiocyanate (also called potassium sulphocyanide) 5% solution in water.

**Procedure when copper and chromium are absent:-**

Weigh 0.5000 gm. sample into a 200 ml. casserole. Add 10 ml. of the nitric-sulphuric acid mixture. Heat over a mush-room top burner and evaporate until strong fumes of sulphur trioxide are evolved. Cool. Add 30 ml. of sulphuric-hydrochloric acid and heat gently until the soluble salts are in solution. Cool to room temperature. Filter off the silica, if any, through a close grained filter-paper. Wash the residue with hot water. Evaporate the filtrate to low bulk, about 30 ml., cool and transfer to a colour comparison tube. Introduce into a similar comparison tube a volume of ferric sulphate solution containing approximately the same amount of iron as the sample and 10 ml. of the standard sodium molybdate solution. Add 5 ml. of the 5% solution of potassium thiocyanate from a burette to each of the tubes and mix well. Next add from a burette 10 ml. of stannous chloride solution to each of the tubes. Dilute the more strongly coloured solution with dilute sulphuric acid (1:7) until the colours match.

**Method of Calculation :—**

Suppose 0.5000 gm. sample was taken and 10 ml. of the standard molybdate solution were used and that the colours matched when the standard solution was diluted to 100 ml. and the sample to 30 ml.

10 ml. of standard solution contain  $10 \times 0.0005$  gm. Mo.

This weight of molybdenum is present in 100 ml.

∴ Each ml contains  $\frac{10 \times 0.0005}{100} = 0.00005 \text{ gm. Mo.}$

30 ml. (sample) contain. . . 0.0015 gm. Mo.

0.5 gm. sample contains 0.0015 gm. Mo.

Hence 100 gms. contain 0.30 gm. Mo.

### **Modification of procedure when copper is present :-**

The principle on which the modification is based is that molybdenum thiocyanate is soluble in ether whereas ferrous and cupric chlorides are almost insoluble.

To the solutions in the colour tubes add 5 ml. of ether and mix well for 5-10 seconds. Compare the colours of the lighter ethereal layer floating on the top. Dilute the darker coloured layer with further additions of ether until the colors match. Calculate as before.

A more accurate procedure, particularly with larger percentages of molybdenum than 0.1, consists in treating the standard and the sample solutions with ether in a separating funnel provided with a glass stopper and drawing off the heavier layers and rejecting them. Only the lighter layer is used for the comparison of colour. For greater accuracy the treatment with ether of the heavier layer should be repeated.

Butyl acetate has also been used for dissolving the red coloured compound of molybdenum oxythiocyanate. Its use has the advantage that its boiling point is 126.5°C. as against 34°C. for ether, an important consideration in tropical climates like India. For the purpose of diluting the more strongly coloured solution, butyl acetate must be used as when using ether. The butyl acetate used must be prepared fresh each day as follows: Shake 250 ml. of the butyl acetate with 25 ml.

of the stannous chloride and 5 ml. of the potassium thiocyanate solutions in a separating funnel, draw off the lower layer and discard the same. Use the upper layer.

**Modification of procedure when Chromium is present :—**

Bring the sample ( 0.5000 gm. ) into solution by treatment with 50 ml. dilute sulphuric acid (1:3) in a 200 ml. casserole. Oxidize with 2-3 gm. of ammonium persulphate. Boil for 10 minutes with 3 ml. of dilute hydrochloric acid. Maintain the volume at about 30-40 ml. by additions of distilled water. Cool to room temperature. Transfer to a colour comparison tube and proceed exactly as described on page 183, the only modification being the addition to the standard molybdenum solution in the comparison tube a volume of chromium sulphate solution which contains the same amount of chromium as the sample under test and of ferric sulphate solution which contains the same amount of iron as the sample under test.

**EXPERIMENT 34.**

**Determination of Molybdenum in Steel  
Containing Tungsten and Vanadium.**

**Alternative Method.**

**Principle :—**

Tungsten is separated as tungstic acid ( $\text{WO}_3$ ) by solution of the steel in a mixture of hydrochloric and nitric acids followed by evaporation to low bulk. The tungstic acid is then filtered off. Molybdenum and vanadium remain in solution as  $\text{MoO}_3$  and vanadyl chloride. When this solution is passed through a column of amalgamated zinc granules, both are reduced, the former to  $\text{Mo}_2\text{O}_3$  and the latter to  $\text{V}_2\text{O}_3$ . These are again oxidized back





times with water. Transfer the amalgam to the reductor tube so as to obtain a uniform distribution of the same and so as not to pack the same tight at any point. Fill the tube completely with water.

**Procedure :—**

Proceed exactly as described in Experiment 32 until the excess of  $\text{SO}_2$  has been expelled and the solution is shown to be free from sulphur dioxide as shown thereunder. Titrate at  $70^\circ\text{C}$ . directly with decinormal potassium permanganate solution. Let 'm' ml. be required. Dilute the solution which has been titrated, with water, so that it contains  $2\frac{1}{2}\%$  sulphuric acid. Introduce into the bottle F, shown in the sketch, 25 ml. of Solution No. 3 and run the solution containing molybdenum and vanadium in the oxidized form through the reductor, taking care not to allow air to pass through, keeping the reductor top always full of liquid. Next run 100 ml. of Solution No. 1. Follow this up with 100-150 ml. water. Disconnect the flask and titrate with decinormal potassium permanganate solution. Let 'n' be the number of ml. of decinormal  $\text{KMnO}_4$  required. From the equation given above, calculate the molybdenum and the vanadium separately.

**Blank :—**

Occasionally a blank should be run to determine the purity of the reagents. If the zinc is pure, not more than 0.2 ml. of decinormal potassium permanganate should be consumed.

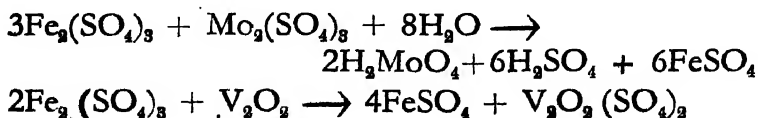
**NOTES :—**

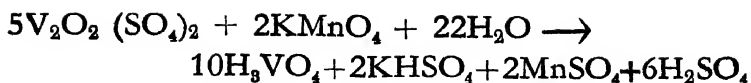
(1) As the reduced solutions are readily oxidized by contact with atmospheric oxygen and by the oxygen of the air present in the filter flask in which the mixture of reduced solution collects it is necessary to absorb them in a solution of ferric sulphate. This gets

reduced to ferrous sulphate in oxidizing molybdenum and vanadium to  $\text{MoO}_3$  and  $\text{V}_2\text{O}_4$  respectively. The mixture of  $\text{FeSO}_4$  and  $\text{V}_2\text{O}_4$  is later titrated by decinormal potassium permanganate solution. The ferrous sulphate formed is slow in undergoing atmospheric oxidation, and, under the conditions of the experiment, the amount so oxidized is negligibly small.

(2) The following will make clear why the number of ml. of 0.1-N potassium permanganate solution required for the oxidation of vanadium, obtained in the first part of the experiment, i.e., by reduction with sulphur dioxide, is multiplied by 3 and then a deduction made from the volume of the same potassium permanganate solution used in the second part of the experiment for obtaining the percentage of molybdenum. The oxidation in the first case is of the compound  $\text{V}_2\text{O}_4$  to  $\text{V}_2\text{O}_5$ . In the second case, the oxidation is of the compound  $\text{V}_2\text{O}_2$  to  $\text{V}_2\text{O}_5$ . The latter change will obviously require for the same weight of vanadium three times the volume of 0.1-N potassium permanganate as is required for the former change.

(3) Though the oxidation of  $\text{V}_2\text{O}_2$  to  $\text{V}_2\text{O}_5$  is not brought about directly by potassium permanganate, in effect it is the permanganate that acts as the oxidant. The ferric alum oxidizes  $\text{V}_2\text{O}_2$  to  $\text{V}_2\text{O}_4$  and in this process gets reduced to ferrous sulphate. The ferrous sulphate and the vanadyl sulphate (from  $\text{V}_2\text{O}_2$ ) are ultimately oxidized to ferric sulphate and vanadic acid by potassium permanganate. The reactions that take place may be represented by the following equations:—





(4) The inlet and outlet tubes passing through the cork in F enable suction to be applied whenever required.

(5) The Jones Reductor Method is also available for the determination of iron, titanium and uranium in ores and metallurgical products.

### **Precautions in the use of the Jones Reductor :—**

(1) When not in use, the top must be kept covered with water. Omission to do this is said to result in the formation of hydrogen peroxide, which oxidizes the reduced compounds and vitiates the accuracy of the determination. This same precaution should be observed during a run i.e., the liquid in the enlarged 5" column at the top must not be allowed to fall below the point C. ( See Fig. 13. )

2. When the zinc particles pack, the reductor should be emptied and only the larger particles used for recharging.

3. The zinc may be amalgamated by running a little of mercuric sulphate solution through the reductor.

## **EXPERIMENT 35.**

### **Determination of Copper in Steel**

**Principle:—**The sample of steel is brought into solution in hydrochloric acid, sulphuric acid or, in a mixture of hydrochloric, nitric and sulphuric acids. The solution freed from nitric acid by fuming to  $SO_3$  is treated with hydrogen sulphide or sodium thiosulphate to separate the copper as copper sulphide. The sulphide is purified from molybdenum and the copper finally determined by the 'Iodide Method' which is described in Experiment 59.

**Solutions required :—**Same as in Experiment 13.  
**Standard Solution Required:** Sodium thiosulphate solution. Dissolve 5 gms. in 1000 ml. water and stock in an amber-colored bottle. Fix its strength in terms of copper, after it has aged for two weeks, using electrolytic copper for standardization exactly as described in Expt. 41.

**Procedure :—**The procedure depends upon whether or not the following elements are present in the steel along with copper :—( 1 ) Tungsten and ( 2 ) Molybdenum.

#### **Case I. Tungsten only is present.**

Use a 5 gm. sample and proceed as described in Experiment 31, using proportionately larger quantities of acid mixture for solution. Carry through until a filtrate free from tungstic acid is obtained. Add 20 ml. of sulphuric acid ( 1 : 1 ) to the filtrate which is contained in a casserole and evaporate to fumes of sulphur trioxide. Dissolve the dry mass in 10 ml. of sulphuric acid ( 1 : 1 ) and 50 ml. of water. Filter off any silica that may have separated, collecting the filtrate in a 600 ml. beaker. Dilute to 300 ml. and heat to boiling. To the boiling solution add 50 ml. of a solution of sodium thiosulphate containing 24 gms. in 50 ml. water. Continue boiling for 5-10 minutes by which time the coagulation of the precipitated copper sulphide will be complete. Filter off the sulphide, wash it free of iron salts using very dilute sulphuric acid ( 1 : 10 ) saturated with hydrogen sulphide. Ignite the precipitate and paper in a porcelain crucible at a dull red heat. Cool. Dissolve, with the aid of heat, the ignited oxide in 5-6 ml. dilute nitric acid ( 1 : 1 ) added to the crucible. Transfer the solution to a 200 ml. conical flask ( preferably a conical beaker ), rinse the crucible two or three times with

water and transfer the rinsings to the flask. Dilute with water to a volume of about 100 ml. . Add ammonia ( s.g. 0.90 ) cautiously until a permanent blue colour forms. Next add dilute acetic acid ( s.g. 1.04<sub>1</sub>) until the blue colour disappears and a pale-green solution results. Add to this, when cold, 1-2 ml. glacial acetic acid, 2-3 gms. of potassium iodide and shake until the latter dissolves. Add from a burette standard sodium thiosulphate until a pale yellow colour is seen. Then add 5 ml. starch solution. Destroy the blue colour by further additions of sodium thiosulphate from the burette.

1 ml. sodium thiosulphate solution = 0.00128 gm. Cu.

## **Case II. Tungsten and Molybdenum are both absent.**

**Procedure :—**Dissolve 5 gm. sample in a casserole in 70 ml. of a mixture of acids obtained by mixing 40 ml. of dilute nitric acid of S.G. 1.2 with 30 ml. of dilute sulphuric acid of S.G. 1.2 Evaporate to fumes. Cool. Dissolve in 10 ml. dilute sulphuric acid ( 1 : 1 ), with the aid of heat, dilute with warm water to about 60-75 ml. . Filter off  $\text{SiO}_2$  and collect the filtrate in a 600 ml. beaker. From this point proceed by adding 50 ml. of strong sodium thiosulphate ( 50% ) solution, boiling, filtering and finishing as described under Case I.

## **Case III. Tungsten and Molybdenum are both present.**

The filtrate from the tungstic acid obtained in Case I is proceeded with in exactly the same manner as described thereunder until the ignited residue, consisting of copper oxide and molybdenum oxide, with traces of ferric oxide, is obtained. Heat the residue in the crucible with 2-3 ml. concentrated hydrochloric acid. Transfer the solution to a beaker of about 200 ml. capacity. Add a solution of sodium hydroxide to

the contents of the beaker until the iron and the copper are precipitated. Boil. Filter. Ignite the residue in a porcelain crucible. Cool and weigh. The residue is dissolved in concentrated hydrochloric acid and the iron is precipitated as hydroxide by ammonia and this is filtered off, ignited and weighed. The weight of the iron oxide is subtracted from the total weight of oxides thus obtaining the weight of copper oxide. From this the percentage of copper is calculated.

NOTES :—

( 1 ) The iodide method for the determination of copper is applicable only when interfering metals like iron in the trivalent condition and molybdenum and tungsten in the hexavalent condition, are eliminated. The procedures described have for their object such elimination.

( 2 ) The chlorides of iron, copper and molybdenum when treated with sodium hydroxide solution yield the hydroxides of iron and copper as precipitates, molybdenum remaining in solution as sodium molybdate. The precipitates of iron and copper hydroxides are dissolved in HCl and the solution when treated with excess ammonia yields iron hydroxide as precipitate while copper remains in solution. Instead of the method of obtaining copper by difference as described under Case III, the copper may be determined iodimetrically from the ammoniacal solution.

## EXPERIMENT 36.

### Determination of Aluminium in Steel

**Introductory :—**

Aluminium is introduced in all classes of steel as a deoxidizer, the percentage so introduced being of the order of 0.01%. In steels meant for surface-hardening

by the nitriding process, it is present to the extent of 1.5 to 1.75%. Such steels contain molybdenum also as an alloying element.

**Principle :—**

When a solution containing ferrous sulphate and aluminium sulphate is carefully neutralized with a solution of sodium bicarbonate, aluminium gets precipitated as the hydroxide while a very large part of the iron remains in solution. The precipitate is filtered off, dissolved in hydrochloric acid and then the aluminium is precipitated as aluminium phosphate, the medium being maintained acid with acetic acid by the addition of ammonium acetate. To avoid contamination by iron, manganese, chromium, nickel, etc., which will be precipitated as phosphates, separation by sodium hydroxide is resorted to, prior to precipitation of aluminium. The aluminium phosphate precipitate is filtered off, washed free of sodium and other salts, ignited and weighed. From the weight of the phosphate, the percentage of aluminium is calculated.

**Procedure :—**

Use a 10 gm. sample in the case of ordinary steels and a 2 gm. sample in the case of nitriding steels. For solution, use dilute sulphuric acid (1 : 9) at the rate of 10 ml. per gram of sample plus 10 ml. extra. Weigh out the sample into a 300 ml. Erlenmeyer flask, add the acid, cover with a cover glass, heat gently until everything is in solution. Dilute with 100 ml. of distilled water. Add an 8% solution of sodium bicarbonate from a burette until the acid is neutralized and a permanent precipitate forms. Add 4 ml. more of the bicarbonate solution at this stage. Shake well. Allow the precipitate to settle for a few minutes. Filter off the precipitate. Wash it 4 or 5 times with water. Discard the filtrate and the washings. Dissolve the precipitate.



on the filter-paper in hot dil.  $\text{HCl}$  ( 1 : 1 ) by pouring it repeatedly on the paper. Wash the same with water. Reserve the solution. Ignite the paper with the residue in a platinum crucible. Fuse the ignited residue consisting of alumina, which was originally present in the metal, with 3-4 gms. of potassium pyrosulphate. Add the melt when cold to the hydrochloric acid solution of the hydroxide precipitate.

Add 2-3 ml. of  $\text{SO}_2$  water, boil the solution for 4 or 5 minutes and then add 3-4 ml. of conc. nitric acid. Neutralize the solution with a 10% solution of sodium hydroxide. Transfer the neutralized solution to a tap-funnel and slowly run this solution into a beaker containing 50-80 ml. of the 10% solution of  $\text{NaOH}$ . Boil for 3-4 minutes to coagulate the precipitate. Filter off the precipitate consisting of the hydroxides of iron, chromium, titanium, nickel, etc.. Wash the residue with a 1% solution of  $\text{NaOH}$  until the aluminium in the form of the soluble sodium aluminate is completely carried down into the filtrate. Neutralize the filtrate with dil.  $\text{HCl}$  ( 1 : 1 ) and add 5 ml. in excess. Add 10 ml. of a 10% solution of diammonium hydrogen phosphate. Stir in macerated filter paper. One of 11 cm. dia. No. 40, Whatman brand will do. Add 0.1 ml. of a 0.02% solution of methyl red indicator. Make just ammoniacal by the careful addition of ammonium hydroxide ( S.G. 0.96 ). The solution will turn yellow when ammoniacal. Add dropwise dil.  $\text{HCl}$  ( 1 : 20 ) until just acid. The solution will turn red when the medium is acid. Now add 20 ml. of a 20% solution of ammonium acetate, raise to a boil and maintain at the boiling temperature for about 5 minutes. Allow the precipitate to settle for 1-2 hours. Filter off the precipitate using a 11 cm dia. Whatman No 40 paper. Wash the residue with a 5% solution of ammonium nitrate until free from chlorides.

Slowly burn the filter paper with the precipitate in a porcelain or platinum crucible until the paper is burnt and then ignite at  $1000^{\circ}\text{C}$ . to constant weight. Calculate the percentage of aluminium.

NOTES :—

( 1 ) Dilute  $\text{H}_2\text{SO}_4$  used for dissolving the sample dissolves all the constituents present in steel except aluminium oxide. This residue is brought into solution by the fusion treatment with potassium pyrosulphate.

( 2 ) The addition of sulphurous acid is for the purpose of reducing any chromic acid that may be present in solution. This reagent will reduce any iron present in the ferric condition to the ferrous condition. The subsequent precipitation of iron by  $\text{NaOH}$  requires that it should be present in the ferric condition. The addition of nitric acid brings about the oxidation of iron from the ferrous to the ferric iron.

( 3 ) The precipitation of aluminium as phosphate having the formula  $\text{AlPO}_4$  having no more of  $\text{P}_2\text{O}_5$  than is represented by this formula is secured only under the carefully controlled condition regarding acidity which has been indicated. .

( 4 ) The addition of paper pulp helps the washing of the ppte. .

( 5 ) The precipitate has a tendency to decrepitate on ignition. The heating should therefore be gradual.

(6) In case the percentage of aluminium exceeds one, the precipitate consisting of the hydroxides of iron, chromium, manganese, nickel, etc. should be dissolved in  $\text{HCl}$  and the hydroxides re-precipitated by adding the solution dropwise from a tap-funnel to 100 ml. of  $\text{NaOH}$  solution. The ppte. is filtered off and the filtrate combined with the original filtrate.

The alternative procedure of keeping iron in the ferrous condition and thereby preventing the co-precipitation of iron as ferric phosphate has been found by the chemists of the U. S. Bureau of Standards to have the drawback that the  $\text{SO}_2$  from  $\text{Na}_2\text{S}_2\text{O}_3$ , used for reduction, has a slight solvent action on the aluminium phosphate formed, leading to lower results.

## EXPERIMENT 37.

### Determination of Titanium in Steel.

**Introductory** :—Titanium is introduced in steels in the form either of ferrotitanium or aluminium-titanium for deoxidation. Its introduction has the advantage that the titaniumdioxide formed has not the hardness that the aluminium oxide has, which is formed when aluminium is used as a deoxidizer, and therefore machining of parts deoxidized with titanium is easier.

#### Principle :—

When hydrogen peroxide is added to titanium sulphate, a yellow colour develops. This is due to the formation of pertitanic acid. The intensity of the colour produced is matched with that from a known amount of titanium sulphate solution similarly treated with  $\text{H}_2\text{O}_2$ .

The determination therefore resolves itself into the preparation of titanium sulphate solution, starting from the sample of steel. This is dissolved in hydrochloric acid and sodium chlorate. Titanium goes partly into solution and partly remains as a residue. This is filtered off and ignited. Call this residue 'A'. The filtrate is treated with ammonia, iron being kept in the ferrous condition by treatment with sodium thiosulphate. The precipitate obtained is filtered off. This precipitate 'B' is mixed with 'A', ignited in a platinum crucible and subjected to treatment with  $\text{H}_2\text{O}_2$ .

$\text{SO}_4$  and  $\text{HF}$ . The residue left is fused with  $\text{Na}_2\text{CO}_3$  and  $\text{NaNO}_3$ , the fused mass extracted with water and filtered. The residue is treated with  $\text{H}_2\text{SO}_4$  and this solution contains all the titanium in the form of titanium sulphate. This is made up to 100 ml. in a 100 ml. graduated flask and aliquot portions are taken for treatment with  $\text{H}_2\text{O}_2$  and for the comparison of the colour with that obtained from a known volume of a standard solution of titanium sulphate similarly treated.

**Solutions required :—**

1. Standard Titanium Sulphate Solution :—

Fuse 0.5000 gm. of pure titanium dioxide with 5 gms. of sodium bisulphate in a platinum crucible covered with lid for 20-30 minutes at a dull red heat. Cool to room temperature. Dissolve melt in 100 of dil.  $\text{H}_2\text{SO}_4$  of s.g. 1.2. Make up the solution to 500 ml. in a 500 ml. graduated flask, using  $\text{H}_2\text{SO}_4$  of the same density for diluting and making up to the mark. Preserve in a stoppered bottle.

In the absence of pure titanium dioxide, the following may be used:

(a) Potassium fluotitanate of the formula  $\text{K}_2\text{TiF}_6 \cdot \text{H}_2\text{O}$  :—Weigh 2.7 gms. of the salt into a platinum dish, evaporate three times to copious fumes with conc.  $\text{H}_2\text{SO}_4$ . Each time use about 30-35 ml. of the acid. After the final fuming, cool to room temp. and pour slowly into one litre measuring flask containing about 800 ml. of dil.  $\text{H}_2\text{SO}_4$  of s.g. 1.2. Cool to room temperature and dilute with water to the mark. Transfer the solution to a glass-stoppered bottle after rinsing it two times with the solution.

(b) Alternatively, potassium titanium oxalate may be used. It has the formula  $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{TiOC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . Weigh into a 500 ml. flask 3.70 gms. of the pure air-

dried salt. Add 8 gms. of ammonium sulphate and 100 ml. of conc.  $\text{H}_2\text{SO}_4$ . Heat gradually to boiling point and maintain boiling for 10 minutes. Cool to room temperature. Add the solution to 700 ml. of dil.  $\text{H}_2\text{SO}_4$  of s.g. 1.2 contained in a 1000 ml. graduated flask. Rinse the flask 3 or 4 times with dil.  $\text{H}_2\text{SO}_4$  of the same s.g., transfer the rinsings to the graduated flask and make up to the mark. Stock in a stoppered bottle.

Whichever reagent is used for the preparation of the standard solution, its value per ml. in terms of  $\text{TiO}_2$  must be fixed as follows :—

Pipette off 50 ml. of the solution into a 600 ml. beaker. Dilute to 200 ml. with water. Heat to boiling. Add ammonia of 0.96 s.g. until there is an excess of 2-3 ml. Filter off the precipitate, wash 3 or 4 times with hot water, ignite in a platinum crucible at about  $1150^\circ\text{C}$ ., cool and weigh. Divide the weight of  $\text{TiO}_2$  by 50 to get the value per ml. of the solution.

#### **Procedure :—**

Dissolve 5 gms. of the sample contained in a 600 ml. beaker in 100 ml. of dil.  $\text{HCl}$  of s.g. 1.1. When solution is complete and no more effervescence is seen, add 100 ml. of a 3% solution in water of sodium chlorate, and boil for 10 minutes after the above addition. Filter off the residue and wash it 3 or 4 times with dil.  $\text{HCl}$  (1 : 1), collecting the filtrate and the washings in a 750 or 800-ml. beaker. Reserve the residue 'A'.

Add to the filtrate  $\text{NH}_4\text{OH}$  of s. g. 0.96 until a faint flocculent precipitate is formed. At this stage the solution should react acid to litmus paper. Add 3 ml. of conc.  $\text{HCl}$ , dilute with water to 300 ml. and add 100 ml. of a 30% solution of sodium thiosulphate. Raise to a boil and maintain at the boiling temperature for 10 minutes. Filter off the precipitate and wash it with hot

water. Call this precipitate 'B'. Transfer this with the paper to a platinum crucible and add to this the residue 'A' along with the filter-paper. Slowly char the papers and finally ignite at the full heat of a Teclu burner. Cool. Add 1 ml. of 1 : 1  $\text{H}_2\text{SO}_4$  and 3-5 ml. of  $\text{HF}$ . Heat on the hot plate until  $\text{SiO}_2$  is volatilized and fumes of  $\text{SO}_3$  are evolved. Heat in a muffle furnace so that  $\text{HF}$  is driven off and the sulphates are decomposed completely. Cool to room temp. . Add about 1 gm. of  $\text{Na}_2\text{CO}_3$  and 0.2-0.3 gm. of  $\text{NaNO}_3$  and fuse over a Teclu burner flame for 5 minutes. Cool. Extract with boiling hot water and filter off the residue of sodium meta titanate, wash it free of the following salts :— sodium molybdate and sodium vanadate, using water as wash liquid. Discard the filtrate and the washings. Ignite the residue in a platinum crucible and fuse it when cold with 2-3 gms. of potassium pyrosulphate, Cool. Extract with dil.  $\text{H}_2\text{SO}_4$  of s.g. 1.2 and make up the solution to 100 ml. in a 100 ml. measuring flask. Pipette off 10 ml. into a colour comparison tube, add 3-5 ml. of 3%  $\text{H}_2\text{O}_2$ . Similarly treat 1 ml. of the standard titanium sulphate solution confined in a second colour comparison tube with 3-5 ml. of the same  $\text{H}_2\text{O}_2$ . Dilute the one which has a stronger colour with water until the colours are matched.

NOTES :—

1. As pointed out under the heading 'Principle', the manipulative details described above have for their object the recovery of the small amount of titanium in the undissolved residue and addition of the same to the larger amount present in the solution of the steel sample in  $\text{HCl}$ .

2. The intensity of the colour due to pertitanic acid is very much affected by the presence of compounds of vanadium, molybdenum, etc.. These elements are eliminated by converting them into water-soluble

sodium vanadate and sodium molybdate by fusion with  $\text{Na}_2\text{CO}_3$  and  $\text{NaNO}_3$ .

3. Fusion with  $\text{K}_2\text{CO}_3$  and  $\text{KNO}_3$  will yield potassium titanate which, unlike sodium metatitanate, is soluble in water. The object being the separation of titanium from vanadium and molybdenum, fusion with  $\text{Na}_2\text{CO}_3$  and  $\text{NaNO}_3$  is adopted.

4. The presence of even very small amounts of H F interferes with the intensity of the yellow colour. Therefore in preparing the standard solution and the sample solution, great care is taken to expel HF.

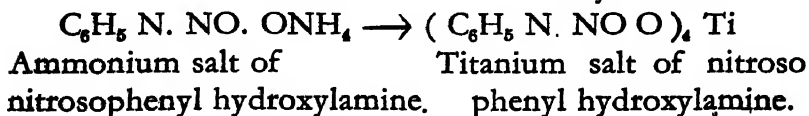
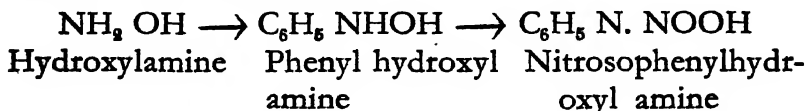
#### EXPERIMENT 37 A. \*

### Determination of Titanium in Steel.

#### Alternative Method.

#### Introductory :—

To shorten the time taken for the determination by the method described in Expt. 37, the following method involving the use of the reagent 'cupferron' has been introduced. This is a short name for the compound having the formula  $\text{C}_6\text{H}_5\text{N} \cdot \text{NOONH}_4$ . This is known as the ammonium salt of nitrosophenyl hydroxylamine. The following scheme indicates how this compound is related to hydroxylamine :—



#### Principle :—

The steel sample is dissolved in dil. HCl. The strongly acid solution which may contain the chlorides of chromium, aluminium, nickel, manganese, vanadium,

molybdenum besides those of iron and titanium, is treated with a water solution of cupferron. Iron and titanium get precipitated. These are filtered off, ignited in a platinum crucible and fused with potassium pyrosulphate. The melt is dissolved in dil.  $\text{H}_2\text{SO}_4$  and the solution treated with  $\text{H}_2\text{O}_2$ . The intensity of the yellow colour produced is matched against that given by a standard solution of titanium sulphate. From the volume of the standard solution, the percentage of titanium is calculated.

### Solutions required :—

( 1 ) Standard Titanium Sulphate Solution :—Same as in Expt. 37.

( 2 ) Cupferron Solution.—Dissolve 2 gms. of the salt in 35 ml. of water. The reagent does not keep well and should be prepared as required.

### Procedure :—

Weigh 0.5 to 1.0 gm. sample of the steel into a 400 ml. beaker. Add 100 ml. of dil.  $\text{HCl}$  ( 1 : 4 ), cover and heat gently until action ceases. Cool the solution to about  $10\text{--}15^\circ\text{C}$ . and add dropwise the cupferron solution, which has been freshly prepared, with constant stirring until the precipitate assumes a reddish brown colour. The titanium compound with cupferron is yellow, while that formed by ferric iron is red. The ferrous salt does not form a precipitate but there is always ferric iron in a solution of the steel sample giving the red-coloured precipitate with the cupferron reagent. When the red-colour appears, stop the addition of the reagent. Stir in ashless filter-paper pulp into the mixture containing the precipitate. Filter off the ppte. through an 11 cm. dia. rapid filter-paper. Wash the ppte. and paper with cold dil.  $\text{HCl}$  ( 1 : 9 ) 10-12 times. Transfer the paper with the ppte. to a large size



platinum crucible. Slowly char the paper and ignite at about  $500^{\circ}\text{C}$ . Cool. Add 1 gm. of potassium pyrosulphate to the ignited residue and fuse over a Bunsen burner flame for 5 minutes. Cool. Dissolve the cold melt in dil.  $\text{H}_2\text{SO}_4$  (1 : 5) and transfer to a 100 ml. graduated flask. Rinse the platinum crucible 3 or 4 times with the same dil.  $\text{H}_2\text{SO}_4$ , make up to the mark with dil.  $\text{H}_2\text{SO}_4$ . Mix thoroughly. Use 20 ml. of the solution for colour comparison. Add 2-3 ml. of  $\text{H}_2\text{O}_2$  and then 3 ml. of  $\text{H}_3\text{PO}_4$ . The comparison tube containing the standard solution must approximately have the same amount of  $\text{H}_3\text{PO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{H}_2\text{O}_2$ , acid, etc., as the solution from which the amount of titanium is to be determined.

NOTES :—

1. The colour due to ferric sulphate must be suppressed by the addition of  $\text{H}_3\text{PO}_4$ .

2. The fusion with  $\text{K}_2\text{S}_2\text{O}_7$  results in the formation of  $\text{K}_2\text{SO}_4$ . This has the effect of decreasing the intensity of the yellow colour. This tendency will be present to the same degree in the standard solution by the addition of like amounts of  $\text{K}_2\text{SO}_4$  and other reagents as in the sample.

(3) If copper is also present in the steel sample, proceed as follows :—Dissolve 0.5 to 1 gm. sample in 30 ml. of dil  $\text{H}_2\text{SO}_4$  (1 : 9). Filter off the insoluble residue. Call this residue  $\text{R}_1$ . Cool the filtrate to about  $10^{\circ}\text{C}$ . and precipitate Ti with cupferron. Filter off the ppt. Ignite it in a platinum crucible at a temperature of  $500^{\circ}\text{C}$ . This residue  $\text{R}_2$  contains the titanium which was present in the original filtrate.

To recover the titanium present in  $\text{R}_1$  proceed as follows :—

Dissolve the residue  $\text{R}_1$  in 25 ml. of dil.  $\text{HNO}_3$  (1 : 2) Add 50 ml. of hot water and ammonia (s.g. 0.96)

until it is in excess. Heat to boiling and filter. Wash the paper and precipitate with hot water. Burn off the paper and add the ignited residue to  $R_2$  and determine the titanium colorimetrically by fusion of the mixed residues with  $K_2S_2O_7$  and treatment with  $H_2O_2$ .

The interference due to the presence of vanadium is overcome as follows :—

Transfer the ignited cupferron precipitate to a platinum dish, add 5 ml. of HF and 10 ml. of  $HClO_4$  and evaporate to a volume of 2-3 ml. Add 50 ml. of water and an excess of ml. of 10% NaOH solution. Boil for several minutes and filter. Wash the residue with water. Ignite the paper with the residue. Fuse with  $K_2S_2O_7$  and determine the titanium from the melt .

Note:  $H_2O_2$  gives a brown colour with  $H_3VO_4$  and thus masks the yellow colour due to pertitanic acid.

### EXPERIMENT 38.

#### Determination of Arsenic in Steel.

##### Introductory :—

This element is not intentionally introduced in steel. In some pig irons this is present, having found its way into the iron from the ore and/or coke. This determination is not carried out as part of the routine analysis of steels. But it is carried out for purposes of investigation of the effect of arsenic on mechanical and other properties of steel.

##### Principle :—

The sample is dissolved in  $HNO_3$ . The excess of it is expelled by evaporation to fumes with  $H_2SO_4$ . The arsenic acid formed is reduced to arsenious acid which is converted into arsenious chloride by liberal addition of HCl. The chloride is distilled off and the distillate absorbed in water. Hydrolysis takes place

and the arsenious acid formed is oxidized to arsenic acid by a standard solution of iodine. From the volume of iodine solution consumed, the percentage of arsenic is calculated.

**Solution Required :—**

Standard Iodine Solution ( Approximately 0.01 N )

Iodine 1.3 gms.

Potassium Iodide 10.0 gms.

Water 1000 ml.

Dissolve the potassium iodide in about 100 ml. water contained in a litre measuring flask. Add the iodine to the solution of potassium iodide. Shake until completely dissolved. Dilute with water and make up to the mark. Fix the strength of the iodine solution against 0.01 N arsenious acid prepared as follows :—Dissolve 0.66 gm. of arsenious acid in 1-litre measuring flask in 30 ml. of a 30% solution of sodium hydroxide. Add HCl of s.g. 1.1 until acid. Test with litmus paper. Cool to room temperature.. Add a saturated solution of sodium bicarbonate so that the acidity due to HCl is destroyed and there is surplus quantity of the bicarbonate solution. A small quantity remaining undissolved at the bottom indicates excess. Pipette off 20 ml. of the arsenious acid into a 250 ml. conical beaker. Add 5 ml. of starch solution ( See Expt. 19 ) to the contents of the beaker. Introduce from a burette the iodine solution until a blue colour is obtained. The reactions taking place during the titration are :—



To prevent the reaction indicated by the lower arrow from taking place, it is necessary to maintain the medium alkaline with sodium bicarbonate. No sodium carbonate or sodium hydroxide should be present.

**Procedure :—**

Dissolve 10 gms. of the steel sample in a 600 ml. beaker in 150 ml. of dil.  $\text{HNO}_3$  (2 : 1), added in small quantities at a time to prevent frothing up and consequent loss. If inadvertent addition of all the quantity of acid at once leads to violent action, moderate the vigour by placing the beaker in a trough of cold water.

Add 50 ml. conc.  $\text{H}_2\text{SO}_4$  and evaporate to dense white fumes. Cool. Rinse the side of the beaker with a jet of cold water to carry down any small amounts of nitric acid. Evaporate a second time to fumes. Cool. Dilute with water to about 50 ml. Transfer the solution to a 1 litre round-bottomed flask fitted up as shown in Fig 14. Introduce 30 gms. of  $\text{FeSO}_4$  or

$\text{Cu}_2\text{Cl}_2$  and 100 ml. conc.  $\text{HCl}$ . Distil off the arsenious trichloride at a temp. not exceeding  $107^\circ\text{C}$ ., absorbing it in a beaker of cold water. When 100 ml. have distilled off, withdraw the beaker. Introduce 50 ml. more of conc.  $\text{HCl}$  and continue the distillation until 50 ml. more have come over as condensate, this being led into the same beaker as before. Withdraw the beaker. Add sodium bicarbonate until the acid formed by hydrolysis is neutralized and there is an excess of it left as

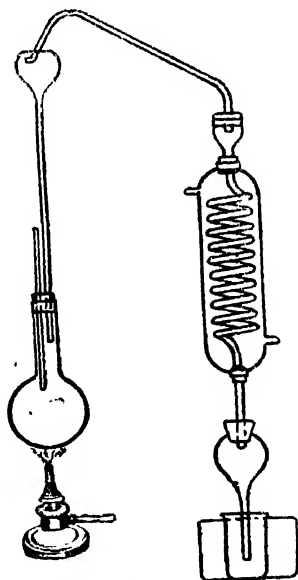


Fig. 14.

solid at the bottom. Cool to room temp. Add 5 ml. of the starch solution and add the standard iodine solution from a burette until a blue colour is obtained.

1 ml. 0.01 N Iodine  $\equiv$  0.000375 gm. As.

## NOTES :—

(1)  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  must not be employed for solution of the steel sample, as arsenic may pass off as arsine (arsenuretted hydrogen). Solution in  $\text{HNO}_3$  yields arsenic acid of the formula  $\text{H}_3\text{AsO}_4$ .

(2) Fuming with  $\text{H}_2\text{SO}_4$  expels the  $\text{HNO}_3$ .

(3)  $\text{FeSO}_4$  or  $\text{Cu}_2\text{Cl}_2$  reduces arsenic acid to arsenious acid.

(4) Sodium hypophosphite or hypophosphorous acid may be substituted for  $\text{FeSO}_4$  or  $\text{Cu}_2\text{Cl}_2$ .

(5) Distilling flasks and other parts are preferably provided with ground-glass joints to avoid vitiation of results by arsenic from the rubber-tubing connections, rubber-corks, etc. . Pure rubber-tubing must be employed when parts with ground glass joints are not available.

(6) A blank should be run for any arsenic that may be present in the reagents and in the glass vessels used. For this purpose, it is advisable to run the blank run first. Introduce 30 gms  $\text{FeSO}_4$  or  $\text{Cu}_2\text{Cl}_2$  into the distilling flask. Add 100 ml. of the conc.  $\text{HCl}$  to be used in the assay and 100 ml. of water. Distil at a temp of  $107^\circ \text{C}$ . Absorb the condensate in water in the beaker. Repeat the distillation, after adding 50 ml. more of  $\text{HCl}$ . When 50 ml. more of the distillate have collected, cool, add the contents of the beaker. to the first distillate, add sodium bicarbonate until there is an excess. Undissolved solid at the bottom of the beaker indicates an excess. Add 5 ml. starch solution and then iodine solution ( 0.01 *N* ) until a blue colour appears. Subtract this volume of iodine solution from that consumed in an actual run on the sample of steel and then calculate.

## EXPERIMENT 39.

**Determination of Nitrogen in Steel**

**Introductory :—**In recent years the determination of gaseous inclusions has assumed very great importance. Those determined are nitrogen, hydrogen and oxygen. Freedom from the last is taken as an indication of quality. Nitrogen introduced in certain classes of steels by the cracking of ammonia gas passed over them maintained at temperatures of  $400-500^{\circ}\text{C}$ . imparts great surface hardness. The determination of the amount so introduced has therefore assumed importance.

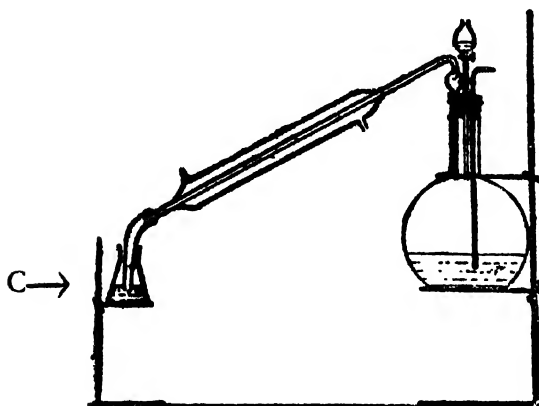


Fig. 15 b.

**Principle:—**

When the steel sample is dissolved in  $\text{HCl}$ , the nitrogen present in it is converted into ammonium chloride. This is subsequently treated with sodium hydroxide and the ammonia liberated is distilled off. The gas is absorbed in a measured excess of a standard solution

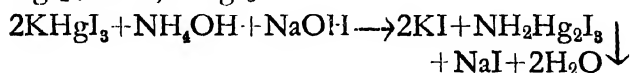
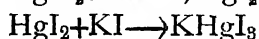
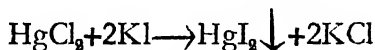
of  $\text{H}_2\text{SO}_4$ . The excess is determined by titration with 0.01 *N*-NaOH. From the volume of acid used up, and the weight of sample taken, the percentage of nitrogen is calculated.

When the amount of nitrogen present is small, of the order of 0.02%, a colour method is employed.

### Special Solutions Required :—

1. 3% NaOH solution.
2. Nessler's Reagent: Dissolve 35 gms. of KI in 200 ml. of water in a 1000 ml. pyrex beaker. Add 200 ml. of a cold saturated solution of  $\text{HgCl}_2$  to the iodide solution. Shake well. To this mixture add with constant stirring and in small quantities at a time the same saturated solution of mercuric chloride until a faint turbidity results. Next add 120 gms. of caustic soda and stir until dissolved. Dilute with water to about 1000 ml. Let stand for a day. Decant off the clear solution into a glass-stoppered bottle and preserve for use in a room free from ammonia and other fumes.

The reactions taking place are :—



3. Dissolve 0.0382 gm. of ammonium chloride of A. R. quality in 100 ml. of distilled water (free from ammonia) in a 1000 ml. measuring flask and make up the same to the mark by adding ammonia-free distilled water.

### Procedure :—

Dissolve 1 gm. of the sample in 20 ml. of dil. HCl (1:1) in a 300 ml. conical flask with the aid of heat, using a water-bath for the purpose. Cool to room temperature.

Pure the solution, when cold, into a distilling flask of the type shown in Fig. 15 a and containing 300 ml. of 3% NaOH solution. Fit up the apparatus as shown in the figure and distil for a period of 40 to 50 minutes receiving the distillate in C. In case the apparatus shown in Fig. 15a is not available, that shown in Fig. 15b may be substituted.

Case I. The sample contains small percentages of nitrogen, being of the order of 0.02%. Transfer the distillate in C to a colour comparison tube. Pipette off 2 ml. of the Nessler Reagent into this tube. Mix well. To a second colour comparison tube forming a pair with the first one, and containing ammonia-free distilled water, add 2 ml. of the Nessler Reagent and then the standard ammonium chloride solution from a burette. Mix well after each addition. Compare the colours. Continue adding ammonium chloride solution until the colours match. As the full colour takes about 15 minutes to develop, it is best to finish off the comparison only after the tubes have stood for this length of time after mixing the solutions.

#### Example and Calculation :—

Weight of steel sample 1 gm.

Volume of standard  $\text{NH}_4\text{Cl}$  solution 10.0 ml.

Bulk of solution in the tube with Std. solution  
40 ml.

Bulk of solution in the tube containing the sample 80 ml.

$$\begin{aligned}\% \text{ Nitrogen} &= 0.00001 \times 10 \times 80 \times 100 \div 40 \\ &= 0.02\end{aligned}$$

Case II. Nitrogen is present to the extent of 0.05 to 1.75%.

Collect the distillate in C containing 50 ml. of 0.02



$N-H_2SO_4$ . Distil for 40-50 minutes. After this interval, pass the distillate into a test-tube containing Nessler Reagent to see if ammonia has ceased to come off. In case there is no more ammonia evolved, titrate the excess of  $0.02\ N-H_2SO_4$  against  $0.02\ N-NaOH$ , using methyl red as indicator. The appearance of a yellow colour marks the end of the reaction.

NOTES :—

(1) Ammonia-free distilled water required for this experiment is obtained by redistilling the distilled water of the Laboratory with caustic soda solution. The first portions of the distillate are discarded ; the later portions only are used.

(2) Caustic soda solution free from ammonia may be made either by dissolving caustic soda of A. R. quality in distilled water and distilling the same until the distillate gives no test for ammonia with Nessler's reagent or it may be prepared by adding sodium metal to distilled water which is then boiled for 10 minutes or until the distillate from the solution gives no test for ammonia with the Nessler reagent.

(3) The value per ml of  $0.02\ N-H_2SO_4$  in terms of nitrogen is found by introducing into the distillation flask containing the solution of the steel sample from which the ammonia has been distilled off, and which has been cooled, temp. to room a known volume of the ammonium chloride solution,  $(No3)$ , distilling absorbing the ammonia evolved in a measured excess of  $0.02\ N-H_2SO_4$  and finding the excess of the acid by titration with  $0.02\ N-NaOH$ , as in the actual run of the steel sample.

(4) It cannot be too strongly emphasised that this determination should be carried out in the Laboratory when free from fumes. This condition is best secured

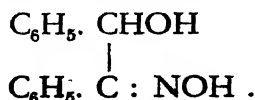
when, in the absence of a separate Laboratory for such work, only this determination and no other is being carried out.

(5) The investigators<sup>1</sup> of this method have pointed out that wrapping up corks with aluminium foil avoids errors due to absorption of ammonia by ordinary corks. Ground-glass joints are most desirable.

#### EXPERIMENT 40—A.

#### Determination of Molybdenum in Steel.

**Introductory :—** A new reagent known as  $\alpha$ -benzoin oxime has been introduced in recent years. The use of an alcoholic solution of this reagent serves very well both for the qualitative detection and the quantitative determination of molybdenum. Its use effects a great saving in time and avoids the unpleasantness of work with hydrogen sulphide whenever separations from interfering elements as in the present case are to be effected. The reagent has the following formula :—



#### Principle :—

When an alcoholic solution of the reagent is added to a sulphuric acid solution containing molybdic acid free from tungstic, vanadic and chromic acids, a white precipitate is obtained. This is filtered off, ignited to  $\text{MoO}_3$  and weighed. From this and from the known weight of sample the percentage is calculated.

#### Solutions Required :—

(1) Dissolve 2 gms. of the reagent in 500 ml. of ethyl alcohol. Filter the solution, if not clear, through a dry filter paper.

<sup>1</sup>Journed of the Iron Steel Institute Vol. No.

(2) 4% boric acid solution in water.

(3) Wash liquid : 50 ml. of No. 1 solution added to about 1000 ml. water containing 10 ml. of conc.  $\text{H}_2\text{SO}_4$ .

**Procedure :—**

Weigh 1–3 gm. sample into a 600 ml. beaker. Add 50 ml. of dil.  $\text{H}_2\text{SO}_4$  (1 : 6), and warm until action ceases. Add 2 to 5 ml. of conc.  $\text{HNO}_3$  to decompose carbides and to oxidize iron and molybdenum. A liberal addition of  $\text{HNO}_3$  would lead to the oxidation of vanadium and chromium, if any. Add 2-4 drops of HF, mix and then 10 ml. of a 4% solution of boric acid. Boil for a few minutes. Filter in case the solution is not clear.

Dilute to 100 ml. with water. Cool to  $25^\circ\text{C}$ . Add about 0.5 gm.  $\text{FeSO}_4$  to reduce vanadic and chromic acids to  $\text{V}_2\text{O}_2(\text{SO}_4)_4$  and  $\text{Cr}_2(\text{SO}_4)_3$ . Cool to  $5^\circ\text{C}$ . and add slowly 10 ml. of the reagent solution and 5 ml. extra for each 0.01 gm. Mo present. Continue to stir the solution, add just enough bromine water to colour the solution pale yellow and then add a few ml. (about 5-10) more of the reagent. Let stand in a cooling mixture of ice and water for 10 minutes. Stir in paper pulp from one 11 cm. dia. paper (Whatman brand No. 40). Filter through a rapid filter. Wash with the wash liquid using about 200 ml. in all. Needle-like crystals appearing in the filtrate indicate excess of the precipitant. According to theory, the formation of the molybdenum complex requires per gram of molybdenum about 14.2 gms. of the reagent for precipitation. A three to fourfold excess is required.

Transfer the paper with the precipitate to a platinum crucible, cautiously dry and then char without allowing the paper to inflame and ignite at a temp. not exceeding  $500^\circ\text{C}$ . Cool in a desiccator and weigh. The ignited

residue may contain small amounts of iron, chromium, etc. To make allowance for these impurities, digest the ignited residue after transferring it to a small beaker (50 ml.) with 5 ml. of  $\text{NH}_4\text{OH}$  (S.G. 0.96) and filter through a small filter. Wash with  $\text{NH}_4\text{OH}$  (1:9), ignite and weigh. Deduct the weight obtained from the original weight. The weight so obtained is that of the pure  $\text{MoO}_3$ . Calculate the percentage.

Tungsten when present in the steel accompanies the molybdenum complex, it also being precipitated as a complex. On ignition it is present as  $\text{WO}_3$ . Digestion with ammonia dissolves both  $\text{MoO}_3$  and  $\text{WO}_3$ . To make allowance for the weight of  $\text{WO}_3$ , proceed as follows:—Add to the filtrate after digesting with ammonia and filtering, 5 ml. of conc.  $\text{H}_2\text{SO}_4$ . Evaporate to fumes. Cool. Dilute to 25 ml. with water, add 1 to 2 ml. of cinchonine solution containing 125 gms. of the base cinchonine in 1000 ml. of dil.  $\text{HCl}$  of s.g. 1.1. Digest at  $80^\circ$ – $90^\circ\text{C}$ . for about 10 hours. Filter through filter paper containing pulp. Wash with dil. cinchonine hydrochloride solution (30 ml. of the above solution in 1000 ml. of water). Transfer the paper to a platinum crucible, char, ignite at  $750^\circ$  to  $850^\circ\text{C}$ ., cool and weigh. Subtract the weight of  $\text{WO}_3$  obtained from the weight of  $\text{MoO}_3 + \text{WO}_3$ . Calculate from the weight of pure  $\text{MoO}_3$  the % of Mo.

#### EXPERIMENT 40—B.

##### Determination of Molybdenum and Vanadium.

(Separations involving the use of Ethyl Ether.)  
Introductory:—The determination of a few constituents in steels based on the solubility of ferric chloride in ether and the insolubility of nickel, manganese, aluminium, chromium and copper chlorides is very attractive. But on account of the ready volatility (b. pt.  $34^\circ\text{C}$ )

and the inflammability of the liquid, it is not generally used in routine analysis. On account rapidity and ease separations involving its use are described here.

### **Solutions Required :—**

1. Dil. HCl ( 1 : 1 )
2. Conc. HCl saturated with ether. Shake 100 ml. of conc. HCl in a separating funnel with small quantities of ether, cooling the funnel under the water-tap after each addition of ether. Continue the addition of ether and cooling under the tap until there is a layer of ether at the top of the heavier layer of the acid-ether solution at the bottom. Draw off this heavier layer into a glass-stoppered bottle and keep in a cool place. About 150 ml. of ether will be dissolved in 100 ml. of the conc. acid.
3. Dil. HCl ( 1 : 1 ) saturated with ether. Proceed as above shaking 100 ml. of dil HCl. ( 1 : 1 ) with small quantities of ether in a separating funnel and cooling under the water-tap until there is a layer of ether at the top. Draw off the lower layer into a glass stoppered bottle and preserve it for use. 100 ml. of the dil. HCl will dissolve about 30 ml. of ether.

### **Procedure :—**

Dissolve 1 gm. sample of steel in a 200 ml. casserole in 15 ml. of dil.  $\text{HNO}_3$  of s.g. 1.2. Evaporate to dryness and bake for 30 minutes. Cool. Dissolve the baked mass in 25 ml. dil HCl ( 1 : 1 ). Boil and filter. Collect the filtrate in a beaker, wash the filter-paper and residue alternately with dil. HCl and warm water until free from iron. Evaporate the filtrate to a volume of about 5 ml. The liquid should be sirupy and no crystals of  $\text{FeCl}_2$  should appear at this stage. Cool the solution and transfer it to the tap-funnel 'a' of the Rothe Extraction Pipette shown in Fig. 16. Draw it into the bulb A. Rinse the

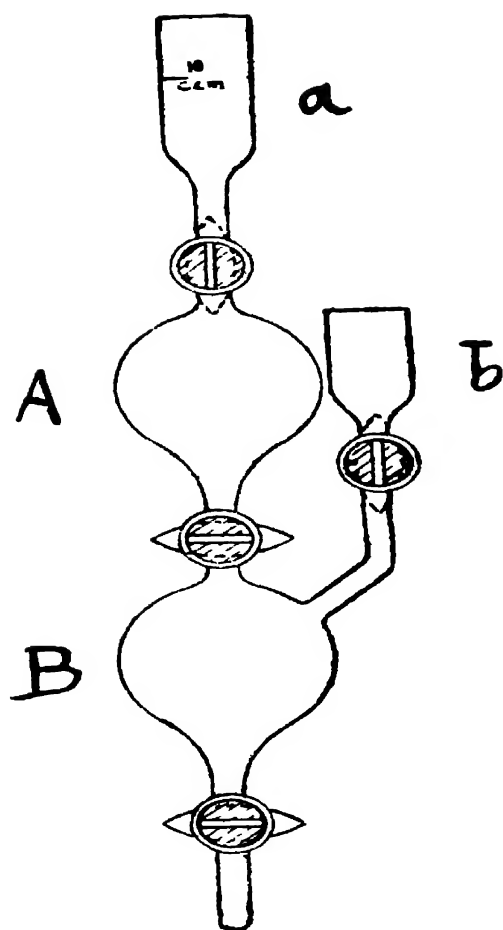


Fig 16 To Face p. 214



beaker 3 or 4 times with dil. HCl (1 : 1) using each time 1 to 2 ml. of the dil. HCl. Add the rinsings to the solution in the bulb A. Cool under the water-tap and add 6 ml. of Solution No. 2. Shake and cool under the tap. Now add about 50 ml. of ether and shake, cooling at the same time under running water from the water-tap. Allow to separate into two layers. Draw off the lower layer into the bulb B. The upper layer i. e. the liquid remaining in the bulb A contains almost all of the iron and the molybdenum present in the steel along with small amounts of the chlorides of nickel, copper, manganese, aluminium, chromium, titanium and vanadium while the bulk of the above chlorides is in the bulb B along with a small amount, about 1% of the Fe and the Mo in the steel. To separate this small amount, introduce via the tap-funnel 'b' about 5-10 ml. of the dil. HCl-ether solution into the bulb B, add about 20 ml. of ether and shake. Draw off the lower layer into a beaker 'V'. To rinse the bore of the tap of B, add 3-5 ml. of the dil. HCl-ether solution via 'b', shake, let stand and draw off the lower layer into the same beaker. Preserve this solution. Draw off the upper layer which is now left in B and which contains the small amount of iron not extracted by the ether solution which remains in bulb A; in a second beaker 'M'. Add via 'a', 3 to 10 ml. of the dil. HCl-ether solution, shake, cool and let stand. Draw off the lower layer into B and then into the beaker 'V'. To rinse the bore of the stop-cock of A, use 2-3 ml. of the dil. HCl-ether solution. Introduce it via 'a', shake, cool and withdraw the lower layer into B and then into the beaker 'V'. This solution contains all the vanadium. Proceed for its determination as follows :— Expel the ether by heating the beaker with its contents on the electric



hot plate or in a hot-water bath and pour into 100 ml. of a hot 10% solution of NaOH. Filter off the hydroxides of Cu, Mn, Ni, Al, Cr, and Ti. Acidify the filtrate with dil.  $\text{H}_2\text{SO}_4$ , add 5-10 ml. of  $\text{SO}_2$ , boil off the  $\text{SO}_2$  and finish by titrating with 0.03 N- $\text{KMnO}_4$  as in Expt. 32.

The layer left in A contains the iron and the molybdenum. Run this into beaker 'M'. For the determination of molybdenum, proceed as follows :— Add 5 ml. of conc.  $\text{H}_2\text{SO}_4$ . Evaporate to fumes. Cool. Cautiously dilute with water to about 75 ml. Heat to boiling, pass a rapid stream of  $\text{H}_2\text{S}$  for 10-15 minutes. Let stand and filter off the molybdenum sulphide. Wash it free of iron salts with 100 ml. of dil.  $\text{H}_2\text{SO}_4$  (1:20) saturated with  $\text{H}_2\text{S}$ . Repeat passing  $\text{H}_2\text{S}$  into the filtrate to ensure complete precipitation. Ignite the  $\text{MoS}_3$  to  $\text{MoO}_3$  at 500-525°C. and weigh.

## **CHAPTER V.**

### **ANALYSIS OF NON-FERROUS ALLOYS.**

#### **EXPERIMENT 41.**

#### **Determination of Copper and Zinc in Brass.**

##### **Outline of Method :—**

The alloy is dissolved in  $\text{HNO}_3$  and evaporated to fumes with  $\text{H}_2\text{SO}_4$ . The sulphates thus obtained are dissolved in water and the copper is precipitated as  $\text{CuS}$  by  $\text{H}_2\text{S}$ . The precipitate is dissolved in  $\text{HNO}_3$  and the Cu determined by electrolysis as in Experiment 43 or by the iodide method as in Experiment 59. From the filtrate zinc is precipitated as zinc ammonium phosphate. This is weighed either as such after filtering off through a Gooch crucible or changed to pyrophosphate by ignition and then weighed. From the weight obtained, the percentage of zinc is calculated.

##### **Procedure :—**

##### **Solution of the Alloy :—**

Dissolve 1 gm. in 10 ml. dil.  $\text{HNO}_3$  (s.g. 1.2) in a 150 ml. covered beaker. Evaporate to fumes with 5 ml. conc.  $\text{H}_2\text{SO}_4$ . Cool. Transfer to a 250 ml. beaker containing 50 ml. water. Rinse the original beaker 4 or 5 times with water and transfer the rinsings to the 250 ml. beaker. Heat to boiling.

##### **Determination of Copper :—**

Pass  $\text{H}_2\text{S}$  for about 20 minutes or until the solution has cooled down to about  $40^\circ\text{C}$ . Filter. Raise the filtrate to boiling point and again pass  $\text{H}_2\text{S}$ . If no precipitate forms, stop passing  $\text{H}_2\text{S}$  but if a precipitate forms, continue passing  $\text{H}_2\text{S}$  for about 5 minutes. Filter through the same filter paper. Repeat passing  $\text{H}_2\text{S}$  until no precipitate is obtained from the filtrate. The preci-

pitate of sulphide on the filter paper must be washed free of zinc. Use  $\text{H}_2\text{S}$  water for the purpose. It is important to keep the precipitate covered with  $\text{H}_2\text{S}$  water during the time taken to free the filtrate from the traces of Cu by passing  $\text{H}_2\text{S}$ . It is best to precipitate all the Cu as  $\text{CuS}$  at one passing of  $\text{H}_2\text{S}$ . The precipitate on the filter paper has a tendency, on exposure to air, to get oxidized to basic sulphate of Cu which is soluble and passes into the filtrate during the subsequent washing of the precipitate. It is necessary therefore to prevent oxidation by covering the precipitate with  $\text{H}_2\text{S}$  water, if all the Cu has not been precipitated at one passing of  $\text{H}_2\text{S}$ . Wash the precipitate 4 or 5 times with  $\text{H}_2\text{S}$  water, transfer the bulk of the precipitate by a jet of water from the wash bottle to a 200 ml. beaker. Use a minimum quantity of water for the purpose. 30-40 ml. of it should suffice. Pour 5 ml. conc.  $\text{HNO}_3$  through the filter paper rolled into a loose lump. Collect the solution in the beaker containing the bulk of the precipitate. Heat to boiling. Pour through the filter paper. Repour through the same until every particle of  $\text{CuS}$  has been dissolved off the filter. Finally wash the funnel and the beaker with water. To the solution add  $\text{H}_2\text{SO}_4$ . Evaporate to fumes and at this stage proceed as shown in Experiment 59.

### Determination of Zinc :—

Boil the combined filtrate and washings from  $\text{CuS}$  to expel  $\text{H}_2\text{S}$ . Neutralize with  $\text{NH}_4\text{OH}$ . Add a slight excess. Introduce 3 gms.  $\text{NH}_4\text{Cl}$ . Add 6 gms.  $(\text{NH}_4)_2\text{HPO}_4$  dissolved in 25 ml. water, and then 1 ml. acetic acid (glacial). Heat to boiling in a water bath. A flocculent precipitate first forms which after 2 or 3 minutes' boiling changes to a crystalline form. Let stand for half an hour. Filter through a Gooch crucible with asbestos pad. Wash with 50% alcohol. ( 1 vol. absolute

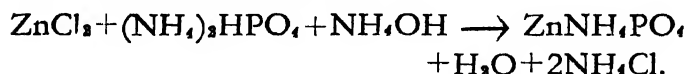
alcohol with 1 vol. water ). Dry at  $110^{\circ}$  to  $120^{\circ}\text{C.}$  to constant weight. Convert the weight of zinc ammonium phosphate into zinc.

Alternatively, the precipitate may be filtered off in the ordinary manner, washed with water, dried and ignited in a porcelain crucible at  $900^{\circ}\text{C.}$  The ignited residue is the pyrophosphate of zinc of the formula  $\text{Zn}_2\text{P}_2\text{O}_7$ . From this, calculate the percentage of zinc.

NOTES :—

1. Zinc ammonium phosphate is soluble both in mineral acids and ammonia.

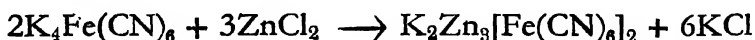
2. The quantity of ammonium phosphate for precipitating Zinc is 20 times that theoretically necessary. The reaction is as follows :—



**Determination of Zinc :—**(Volumetric method.)

The principle of this method consists in the fact that when a solution of potassium ferrocyanide is added from a burette to a solution of zinc chloride, the latter is precipitated as a complex cyanide. The end of the reaction is indicated by the formation of a brown colour on a spotting plate when a drop of uranyl nitrate solution is allowed to mix with a drop from the titration liquid.

The reaction taking place is as follows :—



**Procedure :—**

From the zinc sulphate solution obtained by filtering off  $\text{CuS}$ , expel  $\text{H}_2\text{S}$  by boiling. Add excess of ammonia. Carefully neutralize with dil.  $\text{HCl}$  (1:1). Test with blue litmus paper. Add 3 ml. conc.  $\text{HCl}$ . Keep the volume at about 250 ml. . Heat to boiling. Run the standard potassium ferrocyanide solution ( see below ) into the

boiling hot zinc solution in small quantities, 2-3 ml. at a time. Test with uranyl nitrate solution on the spot-plate. If there is no brown colour, continue the addition of the standard ferrocyanide until the brown colour indication is obtained.

### Standardization :—

1. Potassium Ferrocyanide solution: Dissolve 35 gms. of the salt in 1000 ml. water. Let stand for a week and then fix the value per ml. in terms of zinc as shown below.

2. Uranyl Nitrate solution : Dissolve 2 gms. in 100 ml. water.

**Procedure :—**Weigh 0.2-0.3 gm. pure zinc into a 150 ml. beaker. Dissolve in 10 ml. conc. HCl. Dilute to 50 ml. with water. Make slightly alkaline with ammonia. Neutralize with HCl; add 3 ml. conc. HCl. Transfer to a 500 ml. conical flask. Dilute to about 250 ml. Heat to boiling. Run the ferrocyanide from a burette until a drop of the indicator, on being allowed to mix with a drop from solution in the titration flask, yields a brown colour.

### Blank Test :—

To 200 ml. water in a 500 ml. Erlenmeyer flask add 2 ml. conc. HCl. Neutralize with ammonia. Add 3 ml. conc HCl. Dilute with 50 ml. more water. Heat to boiling. Run the ferrocyanide until a drop from the titration mixture gives a brown colour with a drop of the indicator when they mix on the spotting plate.

### Results of standardization :—

Weight of zinc	= 0.2500 gm.
Vol. of ferrocyanide solution	= 30.3 ml.
“ “ for blank	= 0.3 ml.
30 ml. solution	= 0.25 gm. zinc.
1 ml. solution	$0.25 \div 30$ “ “
	= 0.0083 gm “

## NOTES :—

( 1 ) The method of titration described above is applicable for zinc when the amounts are not small and when the following interfering metals have been removed :—Pb, Cu, Ag, Hg, Cd, As, Sn, Bi, Fe, Cr, Al, Mn and Co.

( 2 ) Correct values can be obtained only by carrying out the assay under conditions of temperature, dilution and acidity similar to those obtained during standardization.

( 3 ) The methods described above assume that only copper and zinc are present in the alloy. This is not always the case. The following scheme holds good for ordinary commercial brass :—

Dissolve 1 gm. of the alloy in 10 ml. conc.  $\text{HNO}_3$  and 10 ml. water. Evaporate to about 10 ml. Redissolve in 20 ml. dil.  $\text{HNO}_3$ . Filter off  $\text{SnO}_2$  through pulp filter. To the filtrate add 10 ml. conc.  $\text{H}_2\text{SO}_4$  and evaporate to fumes. Redissolve in 60 ml. water. Let the precipitate settle. Filter off the lead sulphate through a Gooch crucible with asbestos. Ignite and weigh as  $\text{PbSO}_4$ . Temperature of ignition is  $500^\circ\text{C}$ .

Into the filtrate from  $\text{PbSO}_4$ , pass  $\text{H}_2\text{S}$  to precipitate Cu as  $\text{CuS}$  and determine Cu by electrolysis of the copper sulphate solution. To the liquid from electrolysis, add a few drops of  $\text{HNO}_3$ , then  $\text{NH}_4\text{OH}$  and boil. Filter off the precipitate of  $\text{Fe}(\text{OH})_3$ , if any. Ignite and weigh. To the filtrate, add dimethyl-glyoxime reagent to precipitate nickel, if any is present. Filter off, ignite and weigh as  $\text{NiO}$ . Destroy the excess of the dimethyl glyoxime reagent in the filtrate by boiling with conc.  $\text{HCl}$  until the peculiar smell similar to that of acetic acid is completely removed. Then determine zinc from the liquid as described above by titration or as pyrophosphate.

## EXPERIMENT 42.

**Determination of Beryllium in  
Copper-Beryllium Alloy.****Principle :—**

The alloy is opened out with  $\text{HNO}_3$ . The solution is treated with excess of  $\text{NH}_4\text{OH}$  and filtered. The residue on the paper is  $\text{Be}(\text{OH})_2$ . This is purified by re-solution in  $\text{HNO}_3$  and reprecipitation with  $\text{NH}_4\text{OH}$ .

**Procedure :—**

Dissolve 1 gm. sample contained in a 100-150 ml. beaker in 10 ml. of dil.  $\text{HNO}_3$  (1 : 1). Heat gently until completely dissolved. Transfer to a 400 ml. beaker. Add excess of  $\text{NH}_4\text{OH}$  (1 : 1). Filter. Wash 3-4 times the residue on the paper with 1%  $\text{NH}_4\text{NO}_3$  soln. . Repeatedly extract with 10 ml. of hot dil  $\text{HNO}_3$  (1 : 3) the residue on the paper. Reprecipitate with excess of dil.  $\text{NH}_4\text{OH}$  (1 : 1). Filter, wash with 1%  $\text{NH}_4\text{NO}_3$  solution and ignite the residue with the paper in a platinum crucible, at first gently and then strongly, over a blast lamp. Cool in a desiccator and weigh. Repeat heating, cooling and weighing. Calculate %Be.

## EXPERIMENT 43.

**Analysis of a copper-tin alloy.  
( Copper by Electrolysis. )****Principle :—**

The alloy is opened out with nitric acid. Copper goes into solution as  $\text{Cu}(\text{NO}_3)_2$  and tin is changed into insoluble metastannic acid. The latter is filtered off through a Gooch crucible, washed, dried, ignited and weighed as  $\text{SnO}_2$ . Copper which is present in the filtrate is determined either by the iodide method for which see Experiment 59 or it is determined by electro-deposition. The principle of the latter method consists in the fact that when a current of electricity

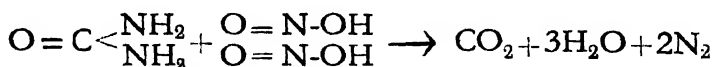
from two or more storage cells is passed through a solution of copper sulphate or copper nitrate, metallic copper is deposited on the cathode. The material of which the electrodes are made is platinum, as this is unaffected by the acidity of the bath that is being electrolysed. The following conditions tending to the production of a bright and firmly adherent deposit in a reasonable length of time must be observed :—

(1) The volume of the solution must not exceed 150 ml.

(2) It must not contain more than 5 ml. of  $N-H_4SO_4$  or  $HNO_3$ .

(3)  $HCl$  must be completely absent from the solution.

(4) When electrolysing a solution acid with  $HNO_3$ , a few milligrams of urea must be added towards the completion of the electrolysis. This serves to destroy any nitrous acid formed and thus eliminates its solvent action on the deposited metal.



(5) The most essential requirement for obtaining a coherent deposit consists in the maintaining of what is known as 'the normal current density' which is defined as the ratio of the current passing through the bath to the area in sq. cms. of the cathode surface. In the assay of copper, the current density which is to be maintained is 0.5 of an ampere for 100 sq. cms. of cathode surface, and 0.5 ampere is referred to as the normal current density in copper assay. As the cathode available in the College has only 30 sq. cms. surface (both the inner and the outer surfaces taken together), more than 0.15 ampere must not be passed through the circuit. The current must be reduced to this value by using a box of resistance in series with the electrolytic bath,



(6) According to Faraday's Laws of Electrolysis, 96,550 coulombs of electricity will deposit  $\frac{63.57}{2}$  or

31.785 gms. of copper. To be able to finish the assay within a reasonable amount of time, it is necessary to start with a weight of alloy which will contain between 0.2-0.4 gm. of Cu. Assuming that there is present 0.4 gm. of Cu in the solution and that only 0.15 ampere current is to be used, the time taken for the deposition of the metal will be

$$\frac{96550 \times 0.4}{31.787 \times 0.15 \times 60 \times 60}$$

hours or nearly 2 hours and 15 minutes.

The time that is actually needed is about 10 hours or more. This is because the ions of copper present in the layer of liquid far removed from the cathode surface move towards it only exceedingly slowly. Also, the current does not remain at the same value throughout the run. It diminishes in strength owing to the increase of the bath resistance, as the metal gets deposited. This also accounts partly for the increased time consumption.

To bring the electrolytic method of assay into more general use, all that is necessary is to remove the above drawbacks. This has been done by the use of a rotating platinum gauze cathode which is also available in the College.

One other condition tending to shorten the time of electrolysis consists in raising the temperature of the bath. This, in the case of the copper assay, is about 60°-70°C. This has the effect of slight stirring and of keeping the cathode surface surrounded by solution of the same strength as at the bottom of the vessel.

#### **Procedure :—**

Weigh 0.5 gm. sample of the drillings into a 200 ml. beaker. Add a mixture of 5 ml. conc.  $\text{HNO}_3$  and

10 ml. water. Cover with a cover glass. Heat on the hot plate until the alloy has completely dissolved. Remove the cover-glass and evaporate to about 5 ml. Add 5ml. conc.  $\text{HNO}_3$ . Digest for 10 minutes on the hot plate. Dilute with 30 ml. of hot water and leave at the corner of the hot plate for an hour. Remove from the hot plate and allow to settle for 10 minutes. Decant through a weighed Gooch crucible with asbestos pad, add 10-20 ml. of hot dil.  $\text{HNO}_3$  (s. g. 1.2) and decant as before. Finally transfer all the residue in the beaker to the crucible by a strong jet of water from the wash-bottle. Wash 4 or 5 times so that the filtrate amounts to about 80-100 ml. . Dry the Gooch crucible in the air oven, place inside a larger crucible, and raise to a dull red heat. Cool and weigh. Calculate the percentage of tin.

NOTES :—

( 1 ) The above method of heating  $\text{SnO}_2$  avoids reduction to Sn by contact with the reducing gases present in the flame.

2. The precipitate of  $\text{SnO}_2$  is contaminated by copper oxide, lead oxide, etc., due to adsorption by stannic acid. When very accurate results are desired, the  $\text{SnO}_2$  must be freed from the above impurities. This is accomplished as follows :—The impure stannic acid is filtered off through filter paper. The residue is ignited and fused with 6 times its weight of a mixture of anhydrous  $\text{Na}_2\text{CO}_3$  and sulphur, mixed in equal proportions, in a porcelain crucible covered with a lid, until the blue flame due to burning sulphur no more appears round the lid. The cooled mass is treated with water in a beaker when  $\text{CuS}$  and  $\text{PbS}$  separate. Sn remains in solution as sodium sulphostannate. The sulphides are filtered off. The filtrate is acidified with acetic acid,  $\text{SnS}_2$  filtered off, ignited and weighed as  $\text{SnO}_2$ .

### Procedure for Copper :—

Evaporate the filtrate from the stannic oxide separation to fumes in a casserole with 5 ml. of conc.  $\text{H}_2\text{SO}_4$ . Cool. Add 30 ml. of water cautiously. Boil for 5-10 minutes. Transfer to a tall 200 ml. beaker. Rinse the dish 3 or 4 times with water and add the rinsings to the beaker. Add  $\text{NH}_4\text{OH}$  of 6 N strength until it is in excess. Acidify with 6N- $\text{H}_2\text{SO}_4$ . Add the acid drop by drop. When the precipitate is dissolved, add only 2 ml. more of the acid and dilute to a volume of about 150 ml.

To find out to which pole of the battery, the cathode previously cleaned, dried, and weighed, is to be connected, dip the two wires from the two poles into a small quantity of acidulated water. That wire which causes the evolution of a larger volume of gas, namely hydrogen, is the one to be connected to the cathode. Two storage cells with a resistance box and a milli-ammeter in series with the bath serve best. Remove the plugs from the box so that a current of about 0.08 ampere passes. Leave overnight. To see if the electrolysis is complete at the end of this time, place about 1 ml. withdrawn from the bath in an inverted porcelain crucible lid. Add a few drops of  $\text{H}_2\text{S}$  water. If no black colouration is produced, the electrolysis is complete ; if there is a black coloration, the operation must be continued for an hour longer and the  $\text{H}_2\text{S}$  water test repeated.

When no black colouration is to be seen, lift the electrodes slowly from the bath without breaking the circuit and directing at the same time a stream of water on to the cathode from the wash bottle. When the cathode is completely above the surface of the bath, break the circuit. Detach the cathode from the binding screw, wash with alcohol, dry above a spirit-lamp flame,

cool in a desiccator and weigh. From the increase in weight, the percentage of copper in the alloy is calculated.

NOTES :—

(1) It is very important that the circuit should not be broken before the cathode is lifted off from the bath. Some of the metal deposited will pass into solution, if this precaution is not observed. Failure to wash during lifting will also result in some of the metal going into solution on breaking the circuit subsequently.

(2) Washing with alcohol and subsequent drying over a spirit lamp flame have for their object the quick drying of the deposit. High temperature and delay in drying lead to oxidation of the deposit.

(3) In the absence of a platinum cathode, one of copper gauze having 20 meshes to the centimetre and 3 cms. in height and 3 cms. in diameter may be made and held by 6" length of No. 16 S. W. G. of copper wire. This wire is tied to the cylindrical copper gauze by wires removed from the same gauze. Such an electrode is suitable only for the deposition of copper. The copper gauze electrode so made is freed from any greasiness by soaking in petroleum ether or ethyl ether for two or three minutes, drying it far above a spirit lamp flame and weighing it. On completion of the deposition, the same precautions have to be observed in removing this from the bath and drying it as in the case of the plain platinum cathode. A higher current density may be used in this case than when a plain platinum cathode is used and a coherent deposit still obtained. Owing to the higher current density the duration of electrolysis is shortened.

(4) The electrolysis should not be continued long after the deposition is complete. Otherwise the deposit turns black. This is due to oxidation.

(5) Should it be found that the operation is not finished at the end of the working day, the assay may be left overnight, reducing the current to a very low value, namely 0.02-0.03 of an ampere.

(6) . The electro-assay of copper may be proceeded with without evaporation to fumes with  $\text{H}_2\text{SO}_4$ . In this case, the nitric acid is neutralized with  $\text{NH}_4\text{OH}$  and only 3-4 ml. of  $\text{HNO}_3$  of 6N strength must be present in 150 ml. of solution ; also, a few milligrams of urea must be added towards the end to prevent the solvent action of the nitrous acid formed during the electrolysis, on the copper deposited. The alloy under examination contains no lead ; but even when this is present, it is not necessary to determine it as  $\text{PbSO}_4$  by evaporation to fumes with  $\text{H}_2\text{SO}_4$ , boiling the residues with water and filtering off  $\text{PbSO}_4$  through a Gooch crucible and weighing it. Proceed as follows :—

Add 15 ml. conc.  $\text{HNO}_3$  to the filtrate from  $\text{SnO}_2$  . Dilute to 350 ml. Electrolyse using a gauze anode of platinum and a current density of 0.5 ampere. Lead is deposited as  $\text{PbO}_2$  on the anode. To ascertain if deposition is complete, expose fresh anode surface and see if it is dimmed. If not dimmed, the deposition is complete. The acid in the bath is neutralised by ammonia until only about 5%  $\text{HNO}_3$  is left, that is, 5 ml.  $\text{HNO}_3$  in 100 ml. and then the electrolysis proceeded with for the deposition of copper, as described at the beginning of the exercise.

### Example I.

#### Case I

Weight of alloy	=0.5 gm.
Weight of Gooch crucible and $\text{SnO}_2$	=15.0621 gm.
Weight of Gooch crucible only	=14.9184 „
Weight of $\text{SnO}_2$	=0.145 „
Hence, % of tin in the alloy	$=0.1445 \times .7881 \times 100 \div 0.5$
	=22.78

Weight of platinum cathode with the deposit of copper	=6.8001 gms.
Weight of the platinum cathode	=5.4200 „
Hence weight of Cu in the alloy	=0.3808 „
Percentage of Cu	=76.16 „

### Case II

Using a copper gauze cathode and the same weight, namely 0.5 gm. of the alloy, the following results were obtained :—

Weight of the cathode+deposit	=4.4047 gms.
Weight of the cathode only	=4.0242 „
Hence, weight of Cu deposit	=0.3805 „
Percentage of Cu	=76.10 „

In each case, the electrolysis was conducted only at the ordinary temperature and a current of 0.05–0.08 ampere only was employed.

Time taken in case I      24 hours.

Time taken in case II    about 18-20 hrs.

The slight red colour of the anode in the above assays is due to the presence of a small amount of manganese in the alloy, as evaporation of the filtrate from  $\text{SnO}_2$  with  $\text{H}_2\text{SO}_4$  gave no weighable amount of Pb as  $\text{PbSO}_4$ .

NOTE :—

Any deposit on the anode, consisting of manganese dioxide and lead dioxide, is removed by dipping it into a solution of  $\text{NaNO}_3$  acidified with dil.  $\text{HNO}_3$ .

### EXPERIMENT' 44.

#### Determination of Nickel in a Nickel Coin.

**Principle :—**

When a solution of dimethylglyoxime in alcohol is added to a neutral or slightly alkaline solution containing  $\text{NiSO}_4$  and  $\text{CuSO}_4$ , the nickel is thrown down as a

voluminous red precipitate. This is slightly contaminated by copper. To remove the small amount of Cu, the precipitate is redissolved in dil.  $\text{H}_2\text{SO}_4$  (s.g. 1.2) and again precipitated by the addition of dimethyl glyoxime, the medium being made neutral or alkaline. The precipitate is filtered off through a Gooch crucible with asbestos felt, dried to constant weight at  $120^\circ\text{C}$ . and weighed. From the weight of the precipitate the % of nickel is calculated.

### **Solutions Required :—**

Dimethylglyoxime Reagent :—See Experiment 28.

### **Procedure :—**

Dissolve a 0.5 gm. sample of the coin in a 150 ml. beaker with 20 ml. dil.  $\text{HNO}_3$  (s.g. 1.2). Add 5 ml. conc.  $\text{H}_2\text{SO}_4$ . Evaporate to fumes. Dilute with 30 ml. water and boil. Cool. Transfer to a 500 ml. measuring flask. Rinse the beaker with water and make up to the mark.

Mix by shaking. Pipette off 100 ml. into a 500 ml. beaker. Make faintly ammoniacal. Test with litmus. Raise to a boil and add 15–20 ml. of the dimethyl glyoxime solution. Let stand on a hot plate at  $50^\circ\text{C}$ . Add ammonia to neutralize the acid formed during the precipitation. The liquid should smell only slightly of ammonia. When the precipitate has been allowed to settle for half of an hour, filter off through filter paper, wash 5 or 6 times by decantation. Dissolve the precipitate on the filter paper by running 15 ml. of hot dil.  $\text{H}_2\text{SO}_4$  (s.g. 1.2) on it and collect the solution in the beaker containing the bulk of the precipitate. Heat until dissolved. Dilute to 200 ml. with water. Neutralize with ammonia. Raise to a boil. Add 10 ml. of the glyoxime reagent. Keep on the hot plate for half an hour. Filter through a Gooch crucible and proceed as in Experiment 28.

**NOTES :—**

(1) When the determination of both Cu and Ni is to be made, the solution is first electrolysed for copper determination in the manner shown in Experiment 43. After the electrolysis is over, nickel is determined by a single precipitation with the glyoxime reagent.

(2) When a sample of german-silver is to be analysed, which is mainly an alloy of nickel and copper, the percentages ranging from 5-20 and 85-70 respectively with varying amounts of tin and zinc, the following scheme will serve :—

Determine Cu and Sn as in Experiment 43.

Determine Ni in the liquid left after electrolysis. In the filtrate from Ni, destroy the dimethyl glyoxime reagent by boiling with 20-30 ml. of dil HCl (s.g. 1.1) until the peculiar smell due to the products of hydrolysis of the glyoxime is no longer noticeable. Neutralize carefully with ammonia and determine zinc as  $Zn_3P_2O_7$  after precipitating it as  $ZnNH_4PO_4$ . See Experiment 41.

**EXPERIMENT 45.**

**Determination of Phosphorus in  
Phosphor-Bronze.**

**Principle :—**

The alloy is dissolved in aqua regia, the heavy metals precipitated by the addition of zinc, the filtrate treated with a little of ferric sulphate and the phosphoric acid precipitated as ferric phosphate by  $NH_4OH$ . The precipitate is filtered off, dissolved in  $HNO_3$ , treated with  $(NH_4)_2MoO_4$  and from the yellow precipitate obtained, P is determined as shown in Experiment 16.

**Solutions Required :— Ferric Sulphate.**

Dissolve 70 gms. ferrous ammonium sulphate crystals in 25 ml. dil.  $H_2SO_4$  (s.g. 1.2) and 50 ml.



water. Add 5–10 ml. conc.  $\text{HNO}_3$ . Boil until oxides of nitrogen are expelled. Cool. Make up to about 100 ml. Use 2 ml. of this solution for each determination. To precipitate 1 gm. P, approximately 1.8 gm. Fe will be required. The solution of ferric sulphate contains 10 gms. Fe.

**Procedure :—**

Dissolve in a 200 ml. basin 1 gm. sample in a mixture of 10 ml conc. HCl and 10 ml. conc.  $\text{HNO}_3$ . Evaporate to dryness. Redissolve in 7 ml. conc. HCl, boil, dilute with cold water to about 30 ml. and introduce a piece of zinc foil or stick. The metals Cu and Sn are precipitated. Filter off the residue, pour on it 3 ml. dil. HCl (1:1) mixed with 3 ml. water. Wash five or six times with water. Boil the filtrate and the washings. Add a drop or two of conc.  $\text{HNO}_3$  and 2 ml. of the Iron solution. Precipitate the iron with excess of  $\text{NH}_4\text{OH}$ . Filter off the mixed precipitate of  $\text{Fe}(\text{OH})_3$  and  $\text{FePO}_4$ , dissolve the precipitate in 20 ml dil.  $\text{HNO}_3$  (s.g. 1.2) and proceed by adding 15 ml. conc.  $\text{HNO}_3$ , heating to  $70^\circ\text{C}$ , adding 40 ml. of ammonium molybdate and finishing off as in Expt. 16.

**NOTES :—**

1. Nitric acid when employed alone for solution of the alloy yields a residue of  $\text{SnO}_2 + \text{P}_2\text{O}_5$ . Only on fusion with KCN this residue yields P as  $\text{K}_3\text{PO}_4$ . From the fused mass the phosphorus can be determined in the following manner :— Dissolve the fusion product in water. Filter off the tin. Acidify the filtrate with HCl in a fume chamber with good draft, expel the free HCN completely by boiling. Neutralize with  $\text{NH}_4\text{OH}$ , add  $\text{HNO}_3$  and  $(\text{NH}_4)_2\text{MoO}_4$ . Treat the yellow precipitate as above. This method has been indicated not to give very satisfactory results by Naish and Clennell.

Moreover, all the P is not obtained with the tin residue unless the amount of tin is sufficient to form stannic phosphate. When deficient, extra tin may be added before dissolving the alloy in  $\text{HNO}_3$  and the residue then proceeded with.

(2) The method of separating the heavy metals by passing  $\text{H}_2\text{S}$  into the solution of the alloy in aqua regia after making it strongly ammoniacal is a rather long one. The method described under *Procedure* is comparatively short. The results obtained by the two methods on a sample containing 0.36% P are in close agreement.

(3) Potassium cyanide and hydrocyanic acid are deadly poisons. Great care is required in handling the former. Solutions from which hydrocyanic acid is expelled by boiling must be boiled in the Fume-chamber.

#### EXPERIMENT 46.

##### Determination of Tin and Lead in Soft Solder.

##### Principle :—

The alloy is dissolved in hot conc.  $\text{HCl}$  with the aid of potassium chlorate when  $\text{PbCl}_2$  and  $\text{SnCl}_4$  are formed. On cooling and dilution, lead chloride separates. This is filtered off. From the filtrate tin determination is made. The principle underlying it is as follows :— Stannic chloride is reduced to stannous chloride when boiled with  $\text{HCl}$  and powdered antimony. The cold, reduced solution of  $\text{SnCl}_2$  is titrated with a standard solution of iodine.

##### Procedure:—

Dissolve 1 gm. sample in 50 ml. conc.  $\text{HCl}$  in a 500 ml. Erlenmeyer flask with the aid of 0.5-1 gm.  $\text{KClO}_3$ . Cool. Dilute to 150 ml. with water. Filter off  $\text{PbCl}_2$ , wash, collecting the filtrate in another 500 ml. conical flask. Add 1-2 gms. of powdered antimony.

Boil vigorously for 5-10 minutes and cool to room temperature. Titrate with a standard solution of iodine as in Experiment 48, pp. 241-242.

NOTES:—

(1) The usual method of dissolving in  $\text{HNO}_3$ , filtering off  $\text{SnO}_2$  which separates and igniting and weighing it, yields accurate results only when the percentage of Sn is about 2. With high percentages as in the case of solder, the method leads to inaccuracy on account of the occlusion by  $\text{SnO}_2$  of a certain amount of lead. The method described overcomes the objection mentioned as the tin is obtained as stannic chloride in solution and is determined by a volumetric process.

(2) 2-3 gms. of mild steel drillings may be substituted for 1-2 gms. of antimony.

(3) Dilution with water to about 300 ml. enables one to catch the endpoint sharply.

When the alloy is boiled with conc.  $\text{H}_2\text{SO}_4$ , Sn passes into solution as stannic sulphate of the formula  $\text{Sn}(\text{SO}_4)_2$  and the lead partly separates as lead sulphate and partly remains in solution. The liquid is diluted with water when  $\text{Sn}(\text{SO}_4)_2$  remains unaffected, the lead sulphate separating out completely as a precipitate. This is filtered off through a Gooch crucible, ignited and weighed. For details see the next Experiment.

NOTE :—

A sample for analysis is obtained in the form of filings by using a medium-cut file. No contamination by iron occurs by this procedure. Clippings take a long time to dissolve.

#### EXPERIMENT 47.

##### **Analysis of Magnolia Metal.**

This is an alloy used as a bearing metal and contains

the following metals: lead, antimony, tin and traces of bismuth and copper.

### Principle :—

When the drillings of the alloy are heated in a Kjeldahl flask with conc.  $\text{H}_2\text{SO}_4$ , sulphates of lead, antimony and tin are formed. The lead sulphate is filtered off through a Gooch crucible, ignited and weighed. The filtrate contains  $\text{Sb}_2(\text{SO}_4)_3$ . On the addition of standard permanganate solution, the antimonious sulphate is oxidized to antimonic acid. The volume of standard  $\text{KMnO}_4$  used is a measure of the amount of antimony present.

The determination of tin is made indirectly by treating separately a second portion of the drillings with dilute  $\text{HNO}_3$  and evaporating to very low bulk, when both the tin and the antimony separate as oxides. These are filtered off, ignited and weighed. From the total weight of  $\text{SnO}_2$  and  $\text{Sb}_2\text{O}_3$ , that of  $\text{Sb}_2\text{O}_3$ , calculated from Sb in the first run, is deducted. From the weight of  $\text{SnO}_2$  the % of tin is calculated.

### Procedure :—

Weigh 1 gm. of the drillings into a 150 ml. Kjeldahl flask with a long stem. Add 30 ml. conc.  $\text{H}_2\text{SO}_4$ . Heat gently at first and then strongly until no dark particles are visible. This takes about 2 hours. Add 15–20 ml. more of conc.  $\text{H}_2\text{SO}_4$  to the cold contents of the Kjeldahl flask. Add cautiously 10–15 ml. of water. Boil for about 20 minutes. Let stand for 10 minutes. Filter through a Gooch crucible with asbestos, using suction and collecting the filtrate in a filter flask. Wash with hot dil.  $\text{H}_2\text{SO}_4$  (sg. 1.2), five or six times. The volume of the filtrate must not exceed 150 ml.  $\text{Sb}_2(\text{SO}_4)_3$  is hydrolysed by a larger dilution than this. If on account of the difficulty of transferring into the crucible all the particles of  $\text{PbSO}_4$ , a larger volume of wash water than

100 ml. is used and a turbidity due to hydrolysis of  $\text{Sb}_2(\text{SO}_4)_3$  appears in the filtrate, remove this by the addition of 10 ml. more of conc.  $\text{H}_2\text{SO}_4$ . The use of a wash-bottle fitted up as shown in Fig. 17 helps the transfer

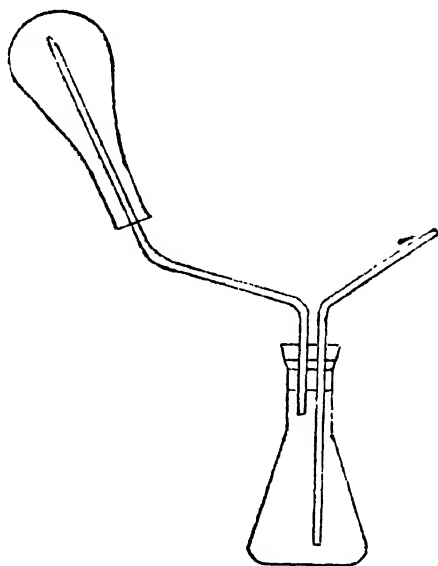
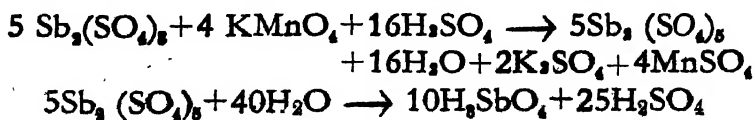


Fig. 17.

of lead sulphate adhering to the Kjeldahl flask. With its use, unnecessary dilution leading to the hydrolysis of  $\text{Sb}_2(\text{SO}_4)_3$  is avoided. Transfer to a 400 ml. beaker the contents of the filter flask. Cool to between  $5^\circ$ - $10^\circ$  C. Add 5 ml. of conc.  $\text{HCl}$  to the contents of the beaker. Run 0.1 N- $\text{KMnO}_4$  from a burette into the beaker until a pink colour persists for half a minute.

1 ml. 0.1 N- $\text{KMnO}_4$  = 0.0061 gm. Sb. . . .

This follows from the following equations :—



2 gm. atoms of Sb as  $\text{Sb}_2\text{O}_3$  require 2 gm. atoms of oxygen for oxidation into  $\text{Sb}_2\text{O}_5$ . 1 ml. 0.1N- $\text{KMnO}_4$  corresponds to 0.0061 gm. antimony.

Ignite the Gooch crucible with  $\text{PbSO}_4$  as follows:—

Cut a hole in an asbestos board of a diameter sufficient for the introduction of the Gooch crucible. The board with the crucible rests on a second porcelain crucible which latter is heated over a burner. This device avoids contact with reducing gases from the flame which will tend to reduce  $\text{PbSO}_4$  to  $\text{PbS}$ .

### **Procedure for joint determination of Sn and Sb:—**

Weigh 1 gm. of the drillings into a 150 ml. beaker. Add 20 ml. of 1.2 s.g.  $\text{HNO}_3$ . Cover with a watch glass. Heat to dryness in a water bath. Bake at  $120^\circ\text{C}$ . for an hour in the air oven or on the hot plate. Cool. Moisten with 3-4 ml. conc.  $\text{HNO}_3$ . Dilute to 30 ml. with water. Digest on the hot plate for 15 minutes and filter through a Gooch crucible with asbestos felt. Wash with hot water until the filtrate is free from acid. Dry in the air oven. Place the Gooch crucible with the dried precipitate of  $\text{Sb}_2\text{O}_4$  and  $\text{SnO}_2$  inside a larger crucible and ignite at a dull red heat for 20 minutes. Cool and weigh.

NOTES :—

(1) To get accurate results the precautions that have to be taken are avoiding a large dilution of the filtrate from  $\text{PbSO}_4$  and the overheating of the dried mass from the evaporation of the nitric acid solution of the alloy for the joint determination of Sb and Sn. Basic nitrates may be formed when the latter precaution is not taken and these will contaminate  $\text{Sb}_2\text{O}_4$  and  $\text{SnO}_2$ , in which case fusion of the residue with  $\text{Na}_2\text{CO}_3$  and sulphur is necessary. The fused mass will consist of thioantimonate and thiostannate of sodium and the sulphides of copper and lead along with sodium poly

sulphide. On treatment with water, the solution appears brown. Addition of a solution of sodium thiosulphate until the brown coloured liquid becomes pale yellow accomplishes the separation of  $\text{CuS}$ ,  $\text{PbS}$ , etc., as precipitates, while  $\text{Sn}$ ,  $\text{Sb}$  remain in solution. Acidification with dil.  $\text{HCl}$  (s.g. 1.1) followed by the passing of a current of  $\text{H}_2\text{S}$  brings down  $\text{SnS}_2$  and  $\text{Sb}_2\text{S}_3$  as precipitates. These are filtered off, washed successively with carbon di-sulphide, and ethyl alcohol, and then ignited. The ignited residues are  $\text{SnO}_2$  and  $\text{Sb}_2\text{O}_3$ .

(2) The titration of the antimonious sulphate in sulphuric acid medium with permanganate is satisfactory only when an excess of permanganate is added and the excess titrated back against ferrous ammonium sulphate. To obviate the necessity for preparing a standard solution of ferrous ammonium sulphate, the titration is carried out after the introduction of conc.  $\text{HCl}$  at the rate of 5 ml. for every 100 ml. of the solution to be titrated. A larger addition than this leads to the evolution of chlorine and a smaller addition leads to incomplete oxidation of  $\text{Sb}_2(\text{SO}_4)_3$ . In either case, the results are not satisfactory. The pink colour obtained in this case is not permanent. But when the addition of  $\text{KMnO}_4$  is stopped after the pink colour persists for 30 seconds, the results are very satisfactory.

(3) Proceed as follows for copper :—Introduce 3 gms. of tartaric acid into the solution in which antimony has been titrated, neutralize with ammonia, and then add 2-3 ml. of  $6N\text{-H}_2\text{SO}_4$ . Add excess of sulphurous acid, boil, introduce 1 gm. of  $\text{KCNS}$  and continue to boil for 10 minutes. Allow the precipitate to settle for 30 minutes. Determine the copper by filtering through a Gooch crucible with asbestos felt, washing it free from  $\text{KCNS}$  with hot water, drying at

105°C. in an air oven to constant weight. From the weight of cuprous thiocyanate  $\text{CuCNS}$ , the % of copper is calculated.

( 4 ) Proceed as follows for bismuth:—Boil 2 gms. sample with 30 ml. conc.  $\text{H}_2\text{SO}_4$  in a Kjeldahl flask until dissolved. Filter off  $\text{PbSO}_4$  through a Gooch crucible. Pass  $\text{H}_2\text{S}$  into the filtrate. Filter off the sulphides, wash with  $\text{H}_2\text{S}$  water, digest the precipitate with freshly prepared  $\text{K}_2\text{S}$  solution in a water bath and filter. Wash, dissolve the residue on the paper consisting of the sulphides of Cu and Bi in dil.  $\text{HNO}_3$ . Add ammonia in excess, neutralize carefully with  $\text{HCl}$ . after introducing into the solution a piece of red litmus paper. When it has become acid, add 1 ml. more of 1.1 s.g.  $\text{HCl}$ . Dilute to 500 ml. and boil. Allow to settle for one hour any precipitate of  $\text{BiOCl}$  that forms. Filter through a Gooch crucible with asbestos felt. Dry in an air oven at 105°C. to constant weight.

$\text{K}_2\text{S}$  solution :— Dissolve 9 gms.  $\text{KOH}$  sticks in 25 ml. water. Take 12 ml. of this in a test-tube and pass  $\text{H}_2\text{S}$  into it until it smells of the gas. Add the remaining 13 ml. of the solution to the solution of  $\text{KHS}$  formed. The resulting solution contains  $\text{K}_2\text{S}$ . Of this, use 10-15 ml. for the experiment.

( 5 ) The results obtained for Pb are accurate only if the conditions laid down regarding the strength of acid, the time of settling before filtering and the temperature of ignition are strictly adhered to. 4 mgms. of lead sulphate dissolve in 100 ml. water at room temperature.

#### EXPERIMENT 48.

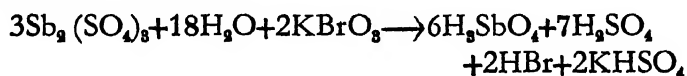
#### Determination of Pb and Sb in White Metal ( Alternative Method ).

**Principle :—**

The alloy is opened out as already described by boiling with concentrated sulphuric acid in a Kjeldahl

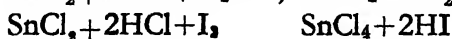
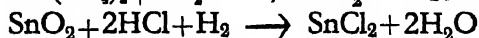


flask. Sulphates of the constituent metals are formed. Of these the sulphate of lead is insoluble. This is filtered off through a Gooch crucible with asbestos as the filtering medium. The determination of antimony present in the filtrate is based on the fact that when a solution of potassium bromate is added to a nearly boiling hot solution of antimonious sulphate, the antimony is oxidized to the pentavalent state. The completion of the oxidation reaction is indicated by the disappearance of the red colour due to the addition of methyl orange, which addition is made at the commencement of the titration. The reaction is represented as follows :—



Tin is determined from the solution left after the titration for antimony. The principle of the determination is based on the reduction of tin from the tetravalent to the bivalent stage by nascent hydrogen resulting from the action of conc. hydrochloric acid on metallic antimony, powdered very fine. The bivalent tin is then titrated against a 0.1-N Iodine solution in the presence of considerable quantity of acid. The completion of the reaction is indicated by the usual starch indicator.

The following are the reactions :—



**Standard Solutions Required :—**

**Potassium Bromate Solution.**

Dissolve 2.7852 gms. of the pure crystals in 1 litre of water. 1 ml. of this solution equals 0.006 gm. antimony.

2. Iodine solution. Same as in Expt. 62 b.

**Procedure :—**

Proceed as in Exp. 47 until the filtrate from lead sulphate is obtained. Transfer the filtrate to a 500 ml. flask and rinse the filter flask two or three times with dil.  $\text{H}_2\text{SO}_4$  (1 : 1). Raise the contents to about  $90^\circ\text{C}$ . Introduce 5 to 6 drops of methyl orange. Add from a burette a standard solution of potassium bromate until the red colour of the solution is discharged. The number of ml. of potassium bromate solution multiplied by the value of the same in terms of antimony gives the antimony content in the weight of the alloy taken.

For the determination of tin, proceed with the solution left after titration for Sb. Add 100 ml. of conc. HCl to the contents of the flask. Introduce 1 gm. of very fine antimony powder (flour antimony) and raise to a boil and boil for 5 minutes. Cool the contents of the flask to room temperature in an atmosphere of carbon-dioxide by passing this gas from a Kipp generator, while keeping the flask in a trough of cold water, which is changed every 3 or 4 minutes. When at room temperature, introduce 2 ml. of freshly prepared starch solution, and then add standard iodine solution from a burette until a blue colour is obtained. The iodine solution having a value of 0.005 gm. tin per ml. is used.

**NOTES:—**

(1) In the absence of potassium bromate of the analytical reagent quality, the exact strength of a solution of the ordinary quality of the same is found as follows :—

Prepare a decinormal solution of potassium antimonyl tartrate by dissolving 16.70 gms. of the salt in exactly 1 litre of water in a graduated flask. Pipette off 20 ml. of this solution into a 300 ml. conical flask. Add 30

ml. of dil  $\text{H}_2\text{SO}_4$  (2 :1). Heat to boiling. Add 4-5 drops of methyl orange and run the potassium bromate solution from a burette until the red colour just disappears. The formula of potassium antimonyl tartrate is  $\text{KSbOC}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ .

(2) Alternatively, the bromate solution may be standardised against pure metallic antimony. Proceed as follows : Dissolve 0.6000 gm. of the pure flour antimony in 20 ml. conc.  $\text{H}_2\text{SO}_4$  in a conical flask. Add 20 ml. of 2:1 dil.  $\text{H}_2\text{SO}_4$  followed by 50 ml. of 10% tartaric acid solution. Boil for 3 minutes to expel any sulphurdioxide that may have formed and that may remain unexpelled. Add 4-5 drops of methyl orange. Add decinormal potassium bromate solution from a burette until the red colour is just destroyed.

(3) For standardisation of iodine solution for use in the determination of tin, see Expt. 62 b.

(4) As any excess of antimony present in the solution of tin does not have any reducing action in the cold on the stannic salt formed, it is not necessary to filter off this excess of antimony before proceeding with the titration of tin.

(5) The solution of stannous chloride is very susceptible to oxidation by atmospheric oxygen. Hence the necessity to cool it down to room temperature in a current of carbon dioxide. It is desirable to keep the gas passing through the solution during the titration also.

### **Determination of Copper in White Metal. ( Alternative Method ).**

#### **Principle :—**

When a solution of sodium hydroxide containing hydrazine hydrochloride is added to the solution of the white metal alloys, copper is precipitated in the metallic form, the other metals remaining completely in solution,

The precipitate is filtered off, dissolved in nitric acid and the determination completed either electrolytically or iodimetrically.

**Procedure :—**

Dissolve 0.5 gm. sample of the alloy in about 15 ml. of aqua regia. When solution is complete, add 15 ml. of water. Strain off the crystals of lead chloride through paper pulp and wash them several times with small quantities of cold water. Add 1 gm. tartaric acid to the filtrate and shake until dissolved. Follow this with the addition of sodium hydroxide solution until nearly neutral. Heat to boiling. Run the hot solution from a tap funnel into a hot mixture of 30 gms. of sodium hydroxide in 250 ml. water containing 2-3 gms. of hydrazine hydrochloride. Stir briskly the latter when the alloy solution is being added. Rinse the tap-funnel 3-4 times with water. Boil for 15 minutes. At the end of this time, the deposit of copper will have separated into dense flocks and the evolution of gas will have ceased. Filter off the copper through paper pulp, and wash well with hot water. Dissolve the deposit in a mixture of equal volumes of dil.  $\text{HNO}_3$  (s.g.1.2) and water. Finish by the Iodide Method. See Expt. 59.

When the determination of antimony only is required, it may be carried out without a preliminary separation of lead. The principle of the method is the same as has already been described. Trivalent antimony is oxidized to the pentavalent condition by a standard solution of potassium bromate.

**Procedure :—**

Dissolve 1 gm. sample in 25 ml. conc. hydrochloric acid in a conical flask. Add occasionally a crystal or two of potassium chlorate to aid solution of the

alloy. Expel the excess of chlorine by boiling. Add 2-3 gms. of sodium sulphite and boil to low bulk when antimony passes to the trivalent condition by the action of sulphurdioxide. Add 50 ml. conc. HCl and about 75 ml. water. Boil 2-3 minutes to get rid of excess of sulphurdioxide. When a piece of filter paper moistened with potassium dichromate solution does not turn green when held in the vapours from the boiling solution, the latter is free from sulphurdioxide. Introduce 3-4 drops of methyl orange and add from a burette the standard potassium bromate solution until the red colour due to the indicator is bleached.\*

NOTE :—

(1) Copper when present in amounts exceeding 3% interferes with the accuracy of the method. In this case, the copper is eliminated as metallic copper by precipitation in an alkaline medium with hydrazine hydrochloride. The deposit is filtered off and the determination of antimony proceeded with by the bromate method using the filtrate for the purpose. Reduction by sodium sulphite and elimination of excess sulphurdioxide is necessary.

(2) Indication of the presence of copper, and the probable amounts of it, is obtained from the green colour of the solution on opening out the alloy.

#### EXPERIMENT 49.

#### Determination of Arsenic, Antimony and Copper in Commercial Copper.

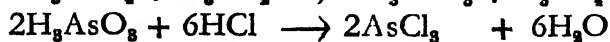
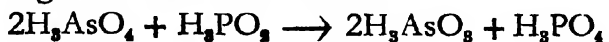
The determination of As, Sb, and Cu only are described below :—

#### Principle :—

The solution of the metal in  $\text{HNO}_3$  yields copper nitrate, arsenic and antimonous acids. A small amount of ferric sulphate solution is introduced into this mixture and the same is carefully neutralized by NaOH

until all the free acid is removed. The solution on dilution, boiling and treating with sodium acetate solution, yields a precipitate containing As, Sb in the form of arsenate and antimonate of iron and the excess of iron as basic ferric acetate. This is filtered off, dissolved in HCl and the solution distilled after treating with hypophosphorous acid or cuprous chloride. The distillate is collected in water. If the temperature of distillation is kept near  $107^{\circ}\text{C}$ , the arsenic trichloride passes off. The residual liquid in the flask contains all the antimony as  $\text{SbCl}_3$ . To it a saturated solution of zinc chloride is added, thereby its boiling point is raised from  $107^{\circ}\text{C}$ . to about  $125^{\circ}\text{C}$ . at which temperature the antimony trichloride passes off as distillate. From the separate distillates obtained, As is determined as  $\text{As}_2\text{S}_3$  and Sb as  $\text{Sb}_2\text{S}_3$  by passing  $\text{H}_2\text{S}$ .

The essential points in the process are the reduction of  $\text{H}_3\text{AsO}_4$  and  $\text{H}_3\text{SbO}_4$  to  $\text{As}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$  respectively by  $\text{H}_3\text{PO}_3$  or  $\text{Cu}_2\text{Cl}_2$  and their conversion into  $\text{AsCl}_3$  and  $\text{SbCl}_3$  by treatment with conc. HCl. Of these,  $\text{AsCl}_3$  distils off at  $107^{\circ}\text{C}$ . and  $\text{SbCl}_3$  distils off at  $125^{\circ}\text{C}$ ., though they distil when present by themselves at much higher temperatures, but in the presence of large amounts of other chlorides such as  $\text{ZnCl}_2$  and HCl, they distil at the temperatures indicated. The following are the reactions taking place during the several stages in the case of arsenic.



Exactly similar reactions take place in the case of antimony.

#### Procedure :—

Dissolve 10 gms. of blister copper in 40 ml. conc.

$\text{HNO}_3$  in a 1000 ml. beaker and boil the solution until a light green solid appears on the surface. Dilute to 500 ml. with water, add 5 ml. ferric sulphate solution containing 3 gms. Fe per 100 ml. solution. Prepare this by dissolving about 21 gms. of ferrous ammonium sulphate crystals in 90 ml. of 1:19  $\text{H}_2\text{SO}_4$  and adding 10 ml. conc.  $\text{HNO}_3$ . Boil this until oxides of nitrogen are expelled. Add the ferric sulphate solution so made.

Add one normal solution of  $\text{NaOH}$  to it, a little at a time and stir well. Stop the addition when the free acid is neutralised as shown by litmus paper. No permanent precipitate should form at this stage. If overrun, and a precipitate appears, add dil.  $\text{HNO}_3$  in drops until the solution clears. Dilute the solution to about 800 ml. with distilled water, add 30 ml. of a saturated solution of sodium acetate, bring to a boil, filter hot through a fluted paper, wash twice with hot water to remove copper. Repeat precipitation of any small amount of As and Sb that may still remain in the filtrate by adding ferric sulphate and proceeding as above. Collect on a separate filter the precipitate obtained on repeating the process. Dissolve the combined precipitates in the least amount of nitric acid. Concentrate the solution to a bulk of 150 ml. . Add a pinch of  $\text{KClO}_3$  and concentrate to 30 ml. Add 30 ml. conc.  $\text{HCl}$ . Repeat evaporation to low bulk to eliminate the nitric acid completely.

Transfer to a 500 ml. round-bottomed flask. Add 5 gms.  $\text{Cu}_2\text{Cl}_2$ . Connect as shown in Fig. 14. Run 100 ml. conc.  $\text{HCl}$  into the flask. Distil until a volume of 150 ml. has collected as distillate. The beaker in which this collects contains 150 ml. of distilled water. Repeat the distillation with 50 ml. more conc.  $\text{HCl}$ , absorbing the distillate in a second beaker contain-

ing 100 ml. distilled water. The volume left in the distilling flask should be about 30 ml. Combine the two distillates, pass  $H_2S$ , filter through a Gooch crucible with asbestos felt, dry at  $100^\circ C$ . and weigh. To the residue in the distilling flask, add 25 ml. of a saturated solution of zinc chloride, and 50 ml conc.  $HCl$  and distil. During the distillation, continue the addition of  $HCl$  from the dropping funnel to keep the volume constant, thereby preventing the separation of crystals.

Neutralise the liquid containing the distillate with ammonia, make slightly acid with  $HCl$  and precipitate  $Sb$  as  $Sb_2S_3$  by passing  $H_2S$ . Filter through a Gooch crucible with asbestos felt. Dry at  $100^\circ C$ . Cool and weigh as  $Sb_2S_3$ . Calculate % of  $Sb$ .

#### NOTES :—

(1) Arsenic may also be determined from the distillate by the volumetric process shown in Experiment 38 when standardising a solution of iodine by arsenious oxide. The free acid is neutralised by sodium bicarbonate and an excess of it is added. The titration with iodine is then made.

(2) Of the two sulphides,  $As_2S_3$  and  $Sb_2S_3$ , the latter is soluble in dil.  $HCl$  (2 : 1) whereas the former is insoluble. Hence the necessity for having only a slightly acid solution for precipitating  $Sb_2S_3$ .

(3) The reagents employed should be the purest obtainable.  $HCl$  may be redistilled and the distillate used for the Experiment. A blank run should also be made and an allowance made for the impurities.

(4) It is best to use a distilling flask with a one-hole ground-in stopper to which is fused the condenser tube. In the absence of this, the rubber tube connections will serve only if the vapours do not come in contact with rubber, Gaseous hydrogen chloride sets



free  $\text{H}_2\text{S}$  from rubber tubing and As appears as  $\text{As}_2\text{S}_3$  in the beaker in which the distillate collects. This should not happen especially when the iodine titration is adopted.

(5) A metallic reducing agent like Zn will lead to the production of  $\text{AsH}_3$  and  $\text{SbH}_3$  which are slightly soluble gases and will pass off unabsorbed.

#### **Procedure for Copper: —**

Dissolve 5 gms. in 10 ml. dil.  $\text{HNO}_3$  (s. g. 1.2) and 1 ml. conc.  $\text{H}_2\text{SO}_4$ , evaporate to fumes, dilute with 15 ml.  $\text{H}_2\text{O}$ , filter off  $\text{PbSO}_4$ . Dilute filtrate to about 50 ml. Add  $\text{Na}_2\text{CO}_3$  until a slight precipitate forms. Add glacial acetic acid until the precipitate dissolves. Add 2-3 ml. more. Make up to 250 ml. Titrate 20 ml. with standard  $\text{Na}_2\text{S}_2\text{O}_3$ , after adding KI. See Expts. 38 and 59.

### **EXPERIMENT 50.**

#### **Analysis of Aluminium Alloys.**

The principles and the procedure for the analysis of duralumin which is typical of this class of alloys are described below. Modifications in the procedure to suit the case of those aluminium alloys in which titanium, nickel, magnesium etc. are absent, will be pointed out.

Duralumin is an alloy containing the following :—

Silicon, Copper, Iron, Aluminium, Manganese, Zinc and Magnesium.

#### **Determination of Silicon :—**

**Principle :—**When the alloy is opened out with a mixture of hydrochloric, nitric and sulphuric acids, silicon is oxidised to silicic acid and the metals are converted into sulphates. The silicic acid is dehydrated on evaporation to fumes of sulphur trioxide. The

residue on evaporation is boiled with dilute sulphuric acid and filtered. The residue on the paper is ignited in a platinum crucible and weighed. By the hydrofluorisation treatment described in Experiment 56 the weight of pure silica is obtained.

**Solutions required :—**

1. **Dilute Sulphuric acid s.g. 1.2.** Pour 250 ml. of conc. sulphuric acid into 750 ml. of cold distilled water.

2. **Acid Mixture :—**Mix 1200 ml. of Solution No. 1 when cold with 600 ml. of HCl ( s.g. 1.2 ) and 200 ml. of  $\text{HNO}_3$  ( s.g. 1.42 ).

**Procedure :—**

Dissolve 1 gm. sample in 30 ml. of the 'Acid Mixture' in a covered casserole. When action has gone on at room temperature for a few minutes and the drillings have dissolved, boil the solution and evaporate to copious fumes of sulphur trioxide. Cool. Dissolve in 100 ml. water and 25 ml. of dil.  $\text{H}_2\text{SO}_4$  ( s.g. 1.2 ). Boil until all the sulphates are in solution. Filter through an ashless filter paper containing paper-pulp. Wash with hot water until free from sulphates. Ignite in a platinum crucible, cool and weigh as  $\text{SiO}_2 + \text{TiO}_2 + \text{Al}_2\text{O}_3$ . Treat the ignited residue with 2-3 ml. of water, 5-10 drops of conc.  $\text{H}_2\text{SO}_4$  and 5 ml. of HF. Evaporate to fumes of  $\text{H}_2\text{SO}_4$ . Ignite strongly. Cool and weigh. From the difference, calculate the percentage of silicon.

**NOTES :—**

( 1 ). In very accurate work, a second evaporation of the filtrate to fumes is necessary to recover the small amounts of silica that remain in solution.

( 2 ) A blank for the silica impurity in the reagents should be run along with the actual run,

(3) A dark coloured residue remaining after the ignition of the silica residue is graphitic silicon. This can only be attacked by fusion with  $\text{Na}_2\text{CO}_3$ . Fuse this with about 2 gms.  $\text{Na}_2\text{CO}_3$  in the same crucible, extract with water, transfer solution to a casserole, add 50 ml. of Solution No. 1, evaporate to fumes, cool, dissolve in 100 ml. water and 10 ml. of Solution No. 1, filter, ignite and weigh and complete as already described.

#### **Determination of Copper :—**

This is determined from the filtrate from silica either by the iodide method or by electrolysis. For the principle of the Iodide method, see Expt. 59. For the Electrolytic method, see Expt. 43.

#### **Procedure for the Iodide method :—**

Heat the filtrate from silica to boiling. Pass a rapid stream of  $\text{H}_2\text{S}$  for 5 minutes. Filter through a low-ash filter paper of 7 cm. diameter. Wash the precipitate of copper sulphide with  $\text{H}_2\text{S}$  water. Ignite in a porcelain crucible. Transfer the cupric oxide to a 250 ml. conical flask. Wash out the crucible with about 5 ml. of hot dil.  $\text{HNO}_3$  (1 : 1). Add 1-2 ml. of conc.  $\text{H}_2\text{SO}_4$ . Evaporate to fumes. Cool. Dissolve in water. Add a solution of  $\text{Na}_2\text{CO}_3$  until the free acid is neutralised and a ppt. of copper carbonate is obtained. Dissolve the precipitate in dilute acetic acid. Add 3-5 ml. of glacial acetic acid, 25 ml. of water, boil gently until every thing is in solution. Cool, add 2-3 gms. of KI and titrate against 0.05 N sodium thiosulphate solution.

**NOTE :—**

In cases where the percentage of copper is very low, a 2-gm. sample should be taken.

#### **Principle of Separation of Copper as a preliminary to the Electrolytic Method :—**

When the alloy is treated with sodium hydroxide solution, aluminium and zinc go into solution as sodium

aluminate and sodium zincate ; copper, iron, manganese and magnesium are unaffected. These are filtered off and dissolved in  $\text{HNO}_3$ . The solution is boiled to expel oxides of nitrogen, sulphuric acid is introduced and then the electrolysis of the solution is carried out.

### Solutions Required :—

1. Dissolve 250 gms. of  $\text{NaOH}$  in distilled water and dilute to 1 litre. Use a Pyrex beaker.

2. Dilute Nitric Acid. Dilute 500 ml. of  $\text{HNO}_3$  (s.g. 1.42) to 1 litre with distilled water.

### Procedure :—

Dissolve 10 gms. of the sample in a 750 ml. beaker using 150 ml. of the  $\text{NaOH}$  solution. As the action is vigorous, add the  $\text{NaOH}$  solution in small quantities at a time. Slow down, if necessary, the vigour of action by surrounding the beaker in which solution is effected, with cold water. Complete the solution by warming. Dilute to 600-700 ml. with boiling hot distilled water. Filter. Wash with water. Dissolve the residue on the paper by pouring 25 ml. of hot  $\text{HNO}_3$  (1 : 1) on it. Collect the solution in a tall form 200 ml. capacity beaker. Wash the filter paper with hot water, boil to expel oxides of nitrogen, introduce 6-8 ml. of 1 : 1  $\text{H}_2\text{SO}_4$  and dilute to about 150 ml. Electrolyse using a current density of 3-5 amperes and a platinum gauze cathode. Ascertain completion of electrolysis by the absence of dark coloration when  $\text{H}_2\text{S}$  water is added to one ml. of the solution withdrawn from the electrolytic bath and introduced into a porcelain crucible. When completed, lower the beaker, without breaking the circuit, and wash the cathode with water. Disconnect, dip the cathode in a large size test tube containing ethyl alcohol or rectified spirit, shake

off the spirit, dry over a small spirit lamp flame. Cool in a desiccator and weigh. Increase in the weight of the cathode is copper.

NOTE :—

Any brown-coloured stain or deposit on the anode is an indication of the presence of lead or manganese or both in the alloy.

### **Determination of Manganese :—**

**Principle :—**See Expt. 22.

**Special Acid Mixture Required** for dissolving the alloy for this determination :—Add slowly 400 ml. of  $H_2SO_4$  (s.g. 1.84) to 200 ml. of water in a beaker. Cool to room temperature. Add 400 ml. of  $HNO_3$  s. g. 1.42. Make up to about one litre with distilled water.

**Procedure :—**

Dissolve 1 gm. sample in 30 ml. of the acid mixture with the aid of heat. When solution is complete, boil off the oxides of nitrogen. Dilute to 100 ml. with boiling hot water, add 10 ml. of  $AgNO_3$  solution and then 30 ml. of the persulphate solution. Heat for 2-3 minutes after the addition of the above. Cool to room temperature. Add from a burette sodium arsenite solution until the pink colour is discharged.

NOTE :—

When the percentage of manganese is high, (i.e.), about 0.5%, use a half-gram sample of the alloy.

### **Determination of Iron :—**

**Principle :—**

The alloy is opened out with  $NaOH$  and filtered. All the iron will be in the residue along with copper, manganese, magnesium with small amounts of aluminium.

The residue is dissolved in  $HCl$  with the help of

bromine.  $\text{Fe}(\text{OH})_3$  contaminated with a small amount of  $\text{Al}(\text{OH})_3$  is precipitated by  $\text{NH}_4\text{OH}$ . The precipitate is filtered off and freed from the adsorbed copper by re-solution in  $\text{HCl}$  and reprecipitation with sodium hydroxide solution followed by filtration. The precipitate is dissolved in  $\text{HCl}$ . The solution is treated with excess of ammonia solution, boiled and filtered. The residue is pure ferric hydroxide. This is ignited and weighed as  $\text{Fe}_2\text{O}_3$ . Alternatively, Fe is determined volumetrically. See Expt. 10.

**Procedure :—**

Dissolve a 2 gm. sample of the alloy in 50 ml. of 25%  $\text{NaOH}$  solution in a large size beaker (600 ml. capacity). Slow down if necessary vigour of attack by cooling the beaker in a water-bath. When all the  $\text{NaOH}$  has been added, heat for a few minutes, dilute with boiling hot water to a volume of about 500 ml. Filter. Wash the residue on the paper with water until free from  $\text{NaOH}$ . Pour 15 ml. of 1 : 1  $\text{HCl}$  to which a few drops of bromine water have been added on the filter paper. Receive the solution in a 150 ml. beaker. Repeatedly pour the same acid until the residue is completely dissolved. Wash with water. Add  $\text{NH}_4\text{OH}$  until in slight excess. Boil for a minute. Filter. Wash the residue two times with water. Pour 10 ml. of boiling hot 1 : 1  $\text{HCl}$  on the filter paper. Collect the solution in a 150 ml. beaker. Repeatedly use the same solution to dissolve off  $\text{Fe}(\text{OH})_3$  from the filter paper. Add  $\text{NaOH}$  solution until alkaline. Boil. Filter. Wash the residue on the paper until free from alkali. Dissolve the precipitate in 10 ml. of 1 : 1  $\text{HCl}$ . Add  $\text{NH}_4\text{OH}$  in slight excess. Boil for 1-2 minutes. Filter. Wash free of chlorides. Ignite the precipitate of pure  $\text{Fe}(\text{OH})_3$  in a porcelain crucible and weigh as  $\text{Fe}_2\text{O}_3$ . Calculate % Fe in the alloy.

## Determination of Zinc :—

### Principle :—

The alloy is opened out with NaOH solution and filtered. The filtrate contains all the zinc and very nearly all the aluminium in the alloy as sodium zincate and sodium aluminate. On passing  $H_2S$  through the solution, zinc sulphide is precipitated contaminated with only a small amount of aluminium hydroxide, if the gassing is stopped at the stage when the bubbles of gas escaping from the surface are just coated with a precipitate of  $Al(OH)_3$ . The precipitate is filtered off, and washed free of NaOH with water containing  $Na_2S$ . The precipitate is dissolved in HCl containing a little bromine. It is boiled to expel the bromine and then treated with  $NH_4OH$  in slight excess. The precipitate of  $Al(OH)_3$  is filtered off. The filtrate is made nearly neutral by adding HCl and the zinc precipitated as zinc ammonium phosphate. This is ignited to pyrophosphate and weighed.

### Procedure :—

Operate on 1 to 2 gm. sample, using for solution 25 ml. of 25% NaOH solution per gm. sample. For details of precipitation of zinc as zinc ammonium phosphate, see Expt. 50.

### NOTES :—

(1) The ordinary qualitative procedure for the separation of zinc from aluminium by precipitating the latter as  $Al(OH)_3$  by means of  $NH_4Cl$  and  $NH_4OH$  is open to the objection that the precipitate adsorbs considerable amounts of zinc which it becomes difficult to eliminate completely even by repeating the precipitation twice. The filtrate if proceeded with for zinc gives low values for the same. The procedure described is free from this objection as the precipitation of aluminium

in alkaline solution does not take place at all ; or if it does take place, the amount precipitated is very small.

(2) The volumetric procedure for zinc by titrating with a standard solution of potassium ferrocyanide has not been found to give accurate and concordant results. Hence the precipitation of zinc as  $\text{ZnNH}_4\text{PO}_4$  is preferred.

### **Alternative Method for the Determination of Zinc :—**

In the absence of nickel and manganese, the following procedure as an alternative to that described above may be adopted :—

**Principle :—**The alloy is opened out with a mixture of the three acids,  $\text{HCl}$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , the copper thrown down as copper sulphide by passing hydrogen sulphide, the ppte. filtered off and zinc precipitated from the filtrate by mercuric potassium thiocyanate.

### **Reagents Required :—**

1. Mixed Acids.— Pour 150 ml. of conc.  $\text{H}_2\text{SO}_4$  into 700 ml. of water contained in a flask. Cool. Add 75 ml. of conc.  $\text{HNO}_3$ . Shake. Add 75 ml. of conc.  $\text{HCl}$ . Mix well.

2. Mercuric Potassium Thiocyanate Solution. Dissolve 54 gms. of  $\text{HgCl}_2$ , i. e.  $\frac{1}{5}$  of its gm. mol. wt. in water in a large size flask. Dissolve in a second flask 78 gms. of  $\text{KCNS}$ , i. e.  $\frac{1}{5}$  of four times its gm. mol. wt. in water. Mix the two solutions and dilute to about 1000 ml. Filter the solution before use.

**Procedure :—**Dissolve 1 gm. sample of the alloy in 35 ml. of the mixed acids in a 150 ml. capacity casserole. Heat on a mush-room top burner to hasten solution. Boil down to fuming and fume for 10 minutes. Cool. Dilute to 200 ml. with water and boil



until a clear solution is obtained. Through the hot solution pass a rapid stream of hydrogen sulphide to precipitate any copper. Filter off the combined precipitate of silica and copper sulphide using a No 4 Whatman paper, and collecting the filtrate in a 400 ml. beaker. Wash the precipitate with hydrogen sulphide water containing per 100 ml. 2 ml. of conc.  $\text{H}_2\text{SO}_4$ . Boil down the filtrate to about 60 ml., filter into a small beaker of about 150 ml. capacity, having a mark to indicate a volume of 75 ml. Cool and dilute to the mark. Add 25 ml. of filtered mercuric potassium thiocyanate solution. Stir and let stand overnight. Filter through a Gooch crucible with asbestos packing, wash the ppte. with 2% potassium mercuric thiocyanate solution and finally with water. Dry at a temp. of  $105^\circ$  to  $110^\circ\text{C}$ . Cool and weigh. To convert the weight of the ppte. into zinc multiply by 0.1266. The ppte. is white. A light pink colour may be ignored.

#### NOTES :—

The time taken for an analysis may be shortened by filtering through a weighed Jena 1G4 filter crucible.

In the presence of nickel and/or manganese, proceed as follows .—

Open out a 2 gm. sample of the alloy with 40 ml. of 20%  $\text{NaOH}$ . When the attack is complete and no more action is visible, add 25 ml. of 10%  $\text{Na}_2\text{S}$  solution, dilute to 300 ml., raise to a boil, allow to settle and filter on a pulp pad. Wash residue on the pulp with hot water containing per 100 ml. 1 gm.  $\text{NaOH}$  and 0.5 gm.  $\text{Na}_2\text{S}$ . Reject the filtrate.

Extract the residue which will consist of the sulphide of zinc and the metals Cu, Fe, Pb, Mn, Ni and Mg, with dil.  $\text{HNO}_3$  (1 : 1). Wash with hot water. Collect the extract and wash water in a casserole. Add

5 ml. conc.  $\text{H}_2\text{SO}_4$ . Evaporate to dense fumes. Cool. Dilute with hot water to 250 ml. Heat to boiling. Pass  $\text{H}_2\text{S}$  until saturated. Filter. Wash residue on the paper with  $\text{H}_2\text{S}$  water. Collect the filtrate and wash water in a 400 ml. beaker. Reject the residue consisting of  $\text{CuS}$  and  $\text{PbS}$ , as these have been determined on a portion of the sample opened out at the very outset with a mixture of acids. Proceed with the filtrate as follows :—

Boil off  $\text{H}_2\text{S}$ . Add 1 ml. of conc.  $\text{HNO}_3$ . Boil again to oxidise the ferrous iron to the ferric state. Dilute to 300 ml. Add a few crystals of ammonium persulphate, 5 gms.  $\text{NH}_4\text{Cl}$  and ammonia solution until the medium is ammoniacal. Boil until only a faint smell of ammonia is noticed. By this means  $\text{Mn}$  is precipitated as  $\text{MnO}_2$ . Filter this off on a pulp pad, collecting the filtrate in a 600 ml. beaker. Wash the pad with the residue with hot water containing per 100 ml. 1 gm.  $\text{NH}_4\text{NO}_3$  and 5 ml. of  $\text{NH}_4\text{OH}$  of S. G. 0.90.

Extract the residue consisting of  $\text{Fe}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$  and  $\text{MnO}_2$  with a mixture of 10 ml. dil.  $\text{HNO}_3$  (1:1) and 5 ml.  $\text{H}_2\text{SO}_4$ . Collect the extract in a 400 ml. beaker. Dilute to 100 ml., boil to expel  $\text{SO}_3$ , dilute to 300 ml. and precipitate  $\text{Fe}$ ,  $\text{Al}$  and  $\text{Mn}$  as before by adding ammonium persulphate, ammonium chloride and ammonia. Filter on a pulp pad and collect the filtrate in the beaker in which the first filtrate from  $\text{Fe}$ ,  $\text{Al}$  and  $\text{Mn}$  was collected and evaporated. The double precipitation serves to eliminate any zinc, nickel and magnesium salts adsorbed by the hydroxide precipitate.

Determine  $\text{Mn}$  in the residue as in Expt. 22, after dissolving the same in a mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  and expelling the  $\text{SO}_3$  by boiling.

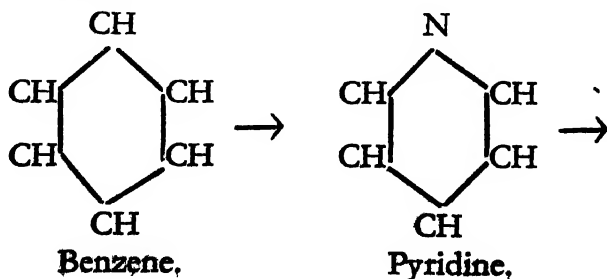
Determine  $\text{Ni}$  from the combined filtrate as

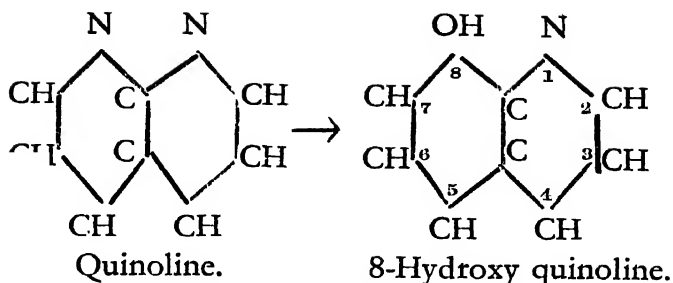
follows:— Destroy the excess of ammonium persulphate by boiling the filtrate with  $\text{H}_2\text{SO}_4$  until the volume is about 250 ml. Add  $\frac{1}{2}$  to 1 gm. ammonium acetate to react with the sulphuric acid resulting from the decomposition of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and the oxidation of  $\text{H}_2\text{SO}_4$ . Make just ammoniacal and precipitate the nickel as the nickel complex by the dimethyl glyoxime reagent and finish as in Expt. 28. Alternatively, filter through a weighed I G 3 Jena crucible, washing with cold water. Dry at  $110^\circ\text{--}120^\circ\text{C}$ . Cool and weigh. The use of this crucible shortens the time taken in making a nickel determination.

### Determination of Magnesium :—

Boil down the filtrate from the nickel complex to about 250 ml., make acid with acetic acid and pass  $\text{H}_2\text{S}$  through the hot solution for 30 minutes. Allow to settle and filter through pulp pad. Wash residue with  $\text{H}_2\text{S}$  water containing 1 to 2 gms.  $\text{NH}_4\text{Cl}$  per 100 ml. Determine Mg from the filtrate as in Expt. 11, i.e. precipitate as  $\text{MgNH}_4\text{PO}_4$ , filter, ignite, cool and weigh as  $\text{Mg}_2\text{P}_2\text{O}_7$ .

The time taken for the Mg determination as  $\text{Mg}_2\text{P}_2\text{O}_7$  may be shortened by the use of a new reagent. This is known as 8—hydroxy quinoline. It has the formula  $\text{C}_9\text{H}_6\text{NOH}$  and is soluble in alcohol and in acetic acid. The following scheme shows how 8—hydroxy quinoline may be supposed to be derived from benzene :—





A 5% solution is used. The precipitate formed with Mg salts has the formula when dried at  $105^{\circ}\text{C}$  ( $\text{C}_9\text{H}_6\text{N.O}$ )<sub>8</sub> Mg,  $2\text{H}_2\text{O}$ . This corresponds to 6.98% Mg. The medium in which the precipitate is formed is ammoniacal. The precipitate on strong ignition changes to  $\text{MgO}$ .

**Procedure :—**

Boil down the filtrate from the zinc sulphide to about 150 ml. Add 25 ml. of a 5% solution of the reagent in alcohol, then 15 ml. of 0.90 s.g. ammonia. Heat just to the boil and let stand on a hot plate for 15 minutes. Filter off the ppte. on a Berlin A 1 crucible, wash with hot water containing per 100 ml. of it 5 ml. of 0.90 s.g. ammonia, ignite, cool and weigh as  $\text{MgO}$ .

**NOTES :—**

The precipitation by means of the reagent can be effected only after the interfering elements like iron, aluminium, manganese, nickel, cobalt and titanium have been eliminated. The solution in which the precipitation takes place will acquire a yellow colour if the reagent is added in excess.

**Procedure for Zinc :—**

Extract the residue of  $\text{ZnS}$  on the pulp filter with 10 ml. of hot 1 : 1  $\text{HCl}$ . Wash with hot water. Add 8 ml. of 1.5 s.g.  $\text{H}_2\text{SO}_4$  and heat to fuming. Cool, dilute to 30 ml., boil and filter into a small beaker. Cool and precipitate zinc as zinc mercuric thiocyanate. Let stand

for 12 hrs. and filter through a weighed Jena I G 4 filter crucible. Wash with 2% mercuric potassium thiocyanate solution, dry at  $110^{\circ}\text{C}$ ., cool and weigh. Factor = 0.1266. The ppte. has the formula  $\text{Zn} [\text{Hg} (\text{CNS})_4]$

## EXPERIMENT 51.

### Determination of Lead in Pig Lead :—

#### Principle:—

When the pig chips are dissolved in dil.  $\text{HNO}_3$ , lead nitrate is formed. This is changed to sulphate by fuming with  $\text{H}_2\text{SO}_4$ . The sulphate is filtered off, dissolved in ammonium acetate and the lead acetate solution obtained is titrated with ammonium molybdate, using tannin solution as the external indicator.

#### Procedure :—

Dissolve 0.3–0.5 gm. in 25 ml. dil.  $\text{HNO}_3$  (s.g. 1.2) in a 150 ml. covered beaker. Evaporate to fumes with 5 ml. conc.  $\text{H}_2\text{SO}_4$ . Pour contents into a 400 ml. beaker containing 50 ml. water, dilute to 100 ml. Filter off the lead sulphate through a filter paper, dissolve ppte. in ammonium acetate and proceed exactly as in Experiment 62c.

#### NOTE :—

The molybdate titration is available only after the removal of interfering elements like Cu and Bi. These are present in pig lead. They remain in solution when  $\text{H}_2\text{SO}_4$  is added, the lead alone being precipitated.

## EXPERIMENT 52.

### Analysis of Spelter.

The chief impurities in spelter are the following :  
Cu, Cd, Pb, Fe, and As.

#### Principle of the Colour Method for Iron :—

When to a solution of  $\text{FeCl}_3$  potassium thiocyanate

solution is added, a blood red colour is produced. The depth of colour is proportional to the quantity of iron present.

**Solutions Required :—**

1. Potassium Thiocyanate :—60 gms. in 1 litre of water.

2. Ferric Chloride. Dissolve 0.07 gm. (70 mgms.) of ferrous ammonium sulphate crystals in 5 ml. dil. HCl (s.g. 1.1). Dilute to 150 ml. Add 0.2%  $\text{KMnO}_4$  solution until just pink. Dilute exactly to 1 litre.

1 ml.  $\text{FeCl}_3 = 0.01 \text{ mgm. Fe.}$

**Procedure for Fe :—**

Dissolve 10 gms. of the sample in 30 ml. conc. HCl and 5 ml. conc.  $\text{HNO}_3$ . Dilute to about 500 ml. with water, heat to  $70^\circ\text{C.}$  and saturate with  $\text{H}_2\text{S}$ , filter (reserve residue  $\text{R}_1$ ), evaporate filtrate to 100 ml., add a drop of conc.  $\text{HNO}_3$  to oxidise ferrous to ferric condition, boil, add  $\text{NH}_4\text{OH}$ , until slightly ammoniacal (test with litmus paper) and filter. Dissolve the ferric hydroxide in 2 ml. dil. HCl (s.g. 1.1). Make up to 200 ml. in a 200 ml. graduated flask. Introduce 20 ml. of the standard  $\text{FeCl}_3$  solution into a colour comparison tube. Into its pair, introduce 20 ml. solution of the sample from the 200 ml. measuring flask. Add to each tube 1–2 mls. of the KCNS soln. . Mix. Hold the two in front of a white sheet of paper pasted to the glass pane of a window. Dilute the darker solution on until it matches the colour of the other.

**Example :—**

At 30 ml. dilution, the sample matched the standard whose volume was 25 ml. It therefore contains :—

0.024% Fe

**Procedure for Pb:—**

Dissolve the residue  $\text{R}_1$  from  $\text{H}_2\text{S}$  treatment in a

mixture of 10 ml. conc. HCl and 5 ml. bromine water. Boil free from bromine, re-precipitate by passing  $\text{H}_2\text{S}$ , filter, wash and dissolve residue in 5 ml.  $\text{HNO}_3$  and 1 ml. bromine, evaporate to fumes with  $\text{H}_2\text{SO}_4$ , cool, dilute, filter off  $\text{PbSO}_4$ , and determine Pb by the molybdate method after dissolving  $\text{PbSO}_4$  in ammonium acetate as in Experiment 62 c.

### **Procedure for Copper :—**

Dilute the filtrate from the lead sulphate precipitate to 150 ml., add 20 ml. conc.  $\text{H}_2\text{SO}_4$ , pass  $\text{H}_2\text{S}$ , filter off  $\text{CuS}$ , wash, dissolve in hot conc.  $\text{HNO}_3$  and proceed by the iodide method as in Experiment 59.

### **Procedure for Cadmium :—**

Neutralise the filtrate from  $\text{CuS}$  with  $\text{NH}_4\text{OH}$ , make just acid with dil. HCl (1:4), pass  $\text{H}_2\text{S}$ , filter off the yellow cadmium sulphide precipitate, dissolve it in a little  $\text{H}_2\text{SO}_4$  (s.g. 1.2), transfer to a weighed platinum dish, evaporate to fumes, ignite at a dull red heat and weigh as  $\text{CdSO}_4$ .  $\text{CdSO}_4$  begins to decompose at  $827^\circ\text{C}$ .

## **Determination of Arsenic.**

### **Principle :—**

When the sample is shaken with copper sulphate solution, zinc sulphate is formed and metallic copper separates out. The arsenic changes by the treatment into a mixture of arsenic and arsenious acids. The former is reduced to arsenious acid by the addition of ferrous chloride in the presence conc. HCl. The mixture is then distilled. When the distillation is carried out at a temperature of  $107^\circ\text{C}$ ., the arsenic trichloride distils off uncontaminated either by antimony or tin chloride. The distillate is hydrolysed by water. On passing  $\text{H}_2\text{S}$  into it, arsenic trisulphide is obtained. This is filtered off, dried and weighed.

**Procedure for Arsenic :—**

Dissolve 20 gms. of the metal in a solution of copper sulphate containing 90 gms. of the salt. Transfer to a distillation flask, 500 ml. capacity, add 10-15 gms. of potassium chloride, 5 gms. ferrous chloride and 50 ml. conc. HCl. Distil off the  $\text{AsCl}_3$  and collect in water in a beaker. Pass  $\text{H}_2\text{S}$  into the distillate, filter off  $\text{As}_2\text{S}_3$  through a Gooch crucible with asbestos felt, dry at  $100^\circ\text{C}$ . and weigh. From the weight of  $\text{As}_2\text{S}_3$ , calculate the % of arsenic. The details for distillation are shown in Expt. 38.

**NOTE :—**

One modification of the procedure consists in treating the sample with potassium bromide and ferric chloride in the presence of HCl and then distilling off the arsenic as the trichloride. The reducing agent in this case is hydrobromic acid from the potassium bromide. The quantities recommended are 8 gms.  $\text{FeCl}_3$  crystals and 3 gms. KBr. per gm. of sample.

**Procedure for Tin :—**

Dissolve 20 gms. of the sample in 100 ml.  $\text{HNO}_3$  (1:1), evaporate to near dryness, add 100 ml. boiling water, filter, wash, dry, ignite and weigh as  $\text{SnO}_2$ .

**Procedure for Zinc :—**

Determine zinc on a 0.5 gm. sample by the volumetric method described in Expt. 41.



# **CHAPTER VI.**

## **ASSAY OF ORES AND BULLIONS OF PRECIOUS METALS.**

### **EXPERIMENT 53**

#### **Determination of Gold in Gold Ore.**

##### **Introductory :—**

The methods which have been described so far are 'wet methods' but the one adopted for gold is known as the 'dry' or 'fire' assay. The fundamental difference in the method now to be described is due to the fact that the gold content of most ores is very small, being, in the case of fairly rich ores, 0.005%. Poorer grades of ore than this have often to be dealt with. To obtain a weighable amount of gold, it is necessary to start with a large quantity of material, about 30 gms., and the operation of treating this for solution by the ordinary 'wet methods' followed by the filtration of the soluble from the insoluble portion is tedious and does not lead to results commensurate with the labour involved. Hence the only method adopted is the one of 'fire-assay'.

##### **Principle of the 'Fire-Assay' :—**

When the ore (60-80 mesh) is fused in a fire-clay crucible with a properly proportioned mixture of sodium carbonate, litharge, charcoal and borax glass, the gangue material consisting of  $\text{SiO}_2$  forms a silicate with  $\text{Na}_2\text{CO}_3$ , which, under the conditions of heating, is in the form of a liquid. The lead monoxide is reduced by the charcoal and the metallic lead formed by the reduction trickles to the bottom of the crucible carrying with it all the particles of gold and any silver that may be present, in the form of an alloy. The function of the borax glass is to thin the slag and combine with the oxides of Cu,





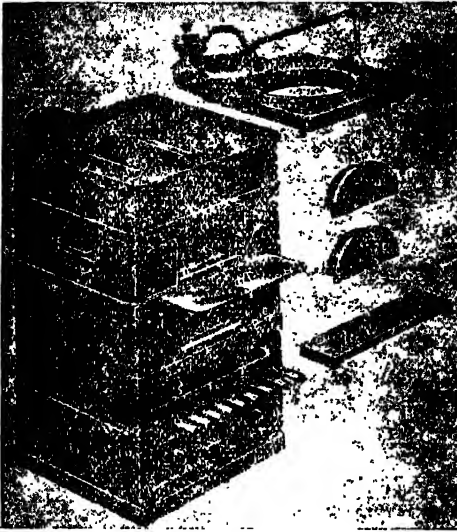


Fig. 18b Portable Assay Furnace.

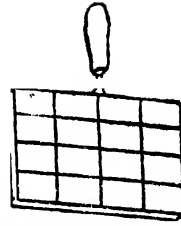


Fig. 18e cupel-tray

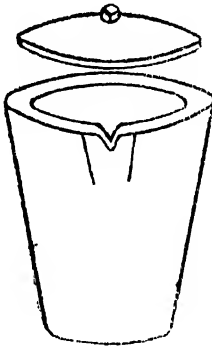
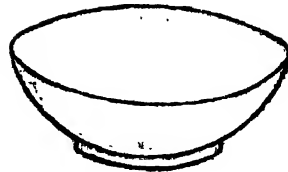


Fig. 18c Fire-clay crucible.



Fig. 18f cupel-mould



ROASTING DISH.

Fig. 18d cupel.

Fig. 18g . .

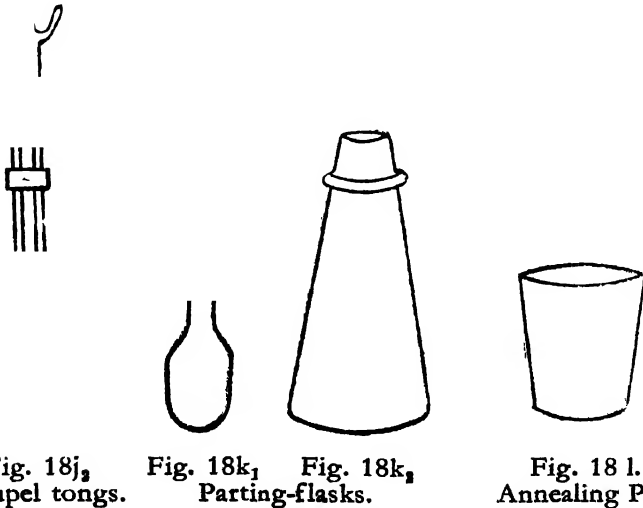
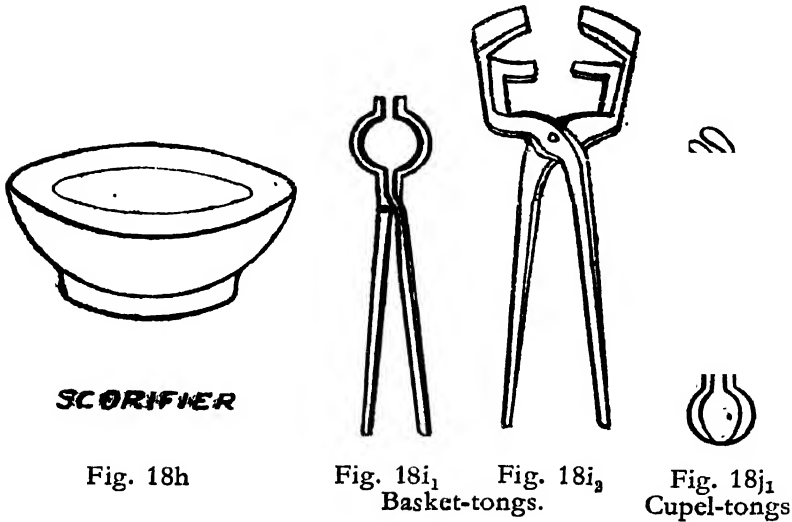
Fe and Mn, that may also be present in the ore, forming the borates of these metals. The mixture of silicates and borates being light floats to the top, and the lead-silver-gold alloy being heavy sinks to the bottom of the crucible. After allowing sufficient time for good separation, the melt (slag and alloy) is poured into a cast iron mould which has been slightly coated over with graphite and warmed. When the same has solidified in the mould, and become cold to the touch, it is removed from the mould and hammered to separate the alloy from the slag. The alloy is then hammered and roughly weighed.

### **Cupellation :—**

The next operation consists in separating the gold and the silver from lead. The process which effects a separation of the two metals, gold and silver, on the one hand, from lead on the other, is known as 'CUPELLATION', on account of the fact that 'CUPELS' are used in the process. These are vessels made of bone-ash. The operation is conducted in a muffle furnace, the temperature of which is at about  $1000^{\circ}\text{C}$ . A cupel is heated in the muffle. Into the hot cupel, the gold-silver-lead alloy, known as a 'lead button', is introduced. It melts and, under the oxidising action of the atmosphere, litharge forms, melts and boils. A large part of this is absorbed by the cupel and a little volatilises. When all the litharge has been absorbed, a bright globule of metal makes its appearance in the cupel. This is then drawn to the mouth of the muffle and covered by a second cupel. When the temperature has fallen to about  $600^{\circ}\text{C}$ ., the cupel is transferred to a cupel-tray and there it is allowed to cool to room temperature. The button of gold and silver is cleaned, with a tooth-brush, free of adhering slag and weighed in a bullion balance.

**Parting :—**

The product of cupellation is an alloy of gold and silver. The determination of each of these is carried out by a process known as 'parting'. The principle of



'parting' is as follows :— when a gold-silver alloy containing three parts of silver to one part of gold is treated with nitric acid, silver dissolves readily leaving

behind gold as a residue. This is transferred to a porcelain crucible, heated to a dull red heat when the yellow colour of gold appears. This is brushed on to one of the pans of a bullion balance and weighed.

The weight of gold subtracted from the weight of gold and silver gives the weight of silver.

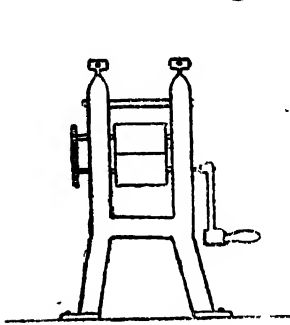


Fig. 18m  
Flattening Rolls.

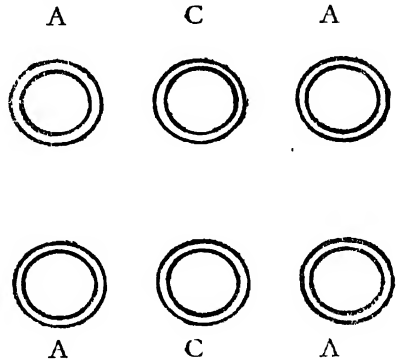


Fig. 18n.  
Disposition of Checks and Assays.

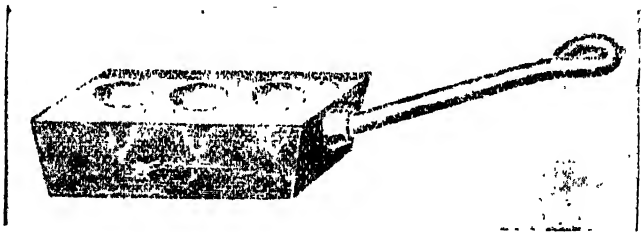


Fig. 18p Button-Mould.

The principles of the fire-assay and the several steps leading to the final form of report have been outlined above. Owing to the high cost of the metals, it is of the utmost importance that the conditions of performing the assay should be so standardised that there will not be any discrepancy when the same material is analysed by two assayers. Some of the conditions, the observance of which is conducive to concordant results by the same assayer or by different assayers working on the same material, are :—

1. A clean separation of the slag from the 'values.' This is brought about by the addition of borax glass to the charge and the correct amounts of lead oxide and charcoal.

2. Maintenance of the proper temperature during cupellation. Too high a temperature leads to volatilisation losses of gold and silver whereas too low a temperature leads to the freezing of the lead oxide and the cupellation does not progress.

3. On account of the volatilisation loss that always occurs, it is necessary to run a 'check' or blank assay, that is to say, a gold-silver alloy is made which approximates in composition to the assay under test, the loss or gain is noted and a corresponding allowance made for the assay under test.

4. 'Parting' will be clean only if the silver in the alloy is 2.5-3 times the weight of gold present. If not present in that proportion, the alloy must be enriched in silver by adding to it pure silver when starting cupellation. The appearance of the cupelled button gives an indication as to whether or not silver is present in the proper proportion. If it has any the slightest yellow sheen, silver must be added. If there is no suggestion of yellow, the alloy will part clean without the addition of silver.

5. The balance used for weighing the gold and the silver is known as the 'bullion balance'. It weighs correct to 1/100 of a milligram.

The following are the weights ordinarily provided in a box of weights suitable for use with this type of balance:—



No. of units	Weight of each	No. of units	Weight of each
1	0.5 gm.	1	10 mgm.
1	0.25 „	2	5.0 „
1	100 mgm.	1	2.5 „
2	50 „	1	1.0 „
1	25 „	2	0.5 „
Material of the rider		Weight of the rider	
gold		5 mgm.	
silver		1 mgm.	
„		$\frac{2}{3}$ „	

6. An allowance must be made for the content of gold and silver that may be present in the litharge used. For this a blank fusion must be run. The charge for the blank is as follows :—

PbO	1 Assay-ton (abbreviated to A.T. which is explained below)
$\text{Na}_2\text{CO}_3$ (anhydrous)	$1\frac{1}{2}$ A. T. (about 50 gms.)
Charcoal	$1\frac{1}{2}$ gms.
Borax glass	$\frac{1}{4}$ A. T. (about 8 gms.)

The melt is poured into a mould and allowed to solidify and cool to about the room-temperature. The slag is hammered off and the lead button cupelled. The button of precious metal, which is silver, is weighed. This is the blank to be allowed for in all assays using the same lot of lead monoxide.

The weight of ore entering into a charge is often expressed in a unit known as the 'Assay-ton'. The object of introducing this term will be clear from the following :—The unit of weight chosen for transactions such as the buying and the selling of precious metals in Europe and America is the ounce Troy. The units of weight used in India for this purpose are the tola and the bharee, divided into mashas and ratties. 1 tola=12 mashas=96 ratties. 1 Bharee=10 mashas=80 ratties.

1 oz. Troy=480 grains.

The values of an ore are to be expressed in ozs. Troy per ton of 2240 lbs. (Avoirdupois).

1 long ton=2240 lbs.

$$=2240 \times 7000 \text{ grains}$$

$$= \frac{2240 \times 7000}{480} \text{ ozs. Troy.}$$

$$= \frac{98000}{3} \text{ or } 32666.6 \text{ ozs. Troy.}$$

If 32.6666 ozs. of ore contain 1/1000 oz. gold, then 1 ton of it will contain one oz. gold.

If 32.6666 gms. of ore contain 1/1000 gm. gold, the value per ton of ore will be 1 oz. gold.

If the weight of ore taken is 32.666 gms. and the weight of gold in it is expressed in mgms., then the number of milligrams also expresses the number of ozs. of gold per ton of ore. Hence the 'Assay-Ton'=32.666 gms.

The other materials entering into a charge are by some writers expressed in gms. and by some in Assaytons. The latter practice arises from the fact that it is convenient to use the box of weights containing multiples and sub-multiples of the assay-ton for weighing the ore as well as the other constituents of the charge.

(2) The ore and the fluxing materials charged into a fire-clay crucible are known as the 'charge'. The ores are either '*straight*' or '*complex*'. Those having quartz as the major gangue material represent the first type while those containing iron pyrites, telluride of gold, stibnite, arsenical pyrites, are complex. Usually the latter type, especially the arsenical ores, require a preliminary treatment before charging into a crucible. Such treatment takes the form of a roast in a fire-clay dish known as a '*scorifier*'.

The nature and the quantity of the fluxing materials are largely determined by the nature and the quantity of the gangue. The following is a table of typical charges for the class of ores mentioned :—

	Quartz or acid ore. 1	Basic or oxidised ore 2	Highly pyritic ore 3	Oorgaum Mines ore. (The Kolar Gold field, Mysore) 4	Column 4 expressed in A.T. 5
Ore	1 A.T.	1 A.T.	1 A.T. ore roast- ed with 15 gms. sand. The roasted product is used.	1000 grains	2 A.T.
Anhydrous Sodium Carbonate }	1.75 A.T.	$\frac{1}{2}$ A.T.	2 A.T.	1368 grains	2.75 A.T.
Litharge	1 "	1 "	$1\frac{1}{2}$ "	460 "	1 A.T.
Charcoal	$1\frac{1}{2}$ gms.	2-5 gms.	2-5 gms.	—	—
Flour (Wheat) }	—	—	—	32 grains	2 gms
Borax glass	$\frac{1}{4}$ A.T.	$\frac{3}{4}$ A.T.	—	—	—
Borax	—	—	1 A.T.	640 grains	1.3 A.T.
Silver Nitrate }	—	—	—	2.5 "	10 ml.
					0.1 N- strong

To avoid having to add silver and then cupel, preliminary to parting, it is sometimes added in the form of silver nitrate solution to a crucible charge.

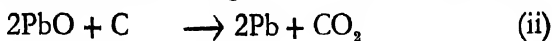
This is possible only when dealing with known ores. With strange or unknown ores, a preliminary assay is necessary to decide whether silver nitrate is to be added or not to the crucible charge to obtain a gold-silver button, after cupellation, of satisfactory composition for successful and correct parting.

The quantities of chemicals to be calculated for a charge are obtained from the following reactions :—



106 gms. 60 gms.

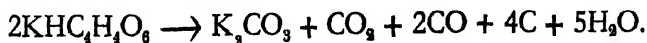
As 60 gms. of silica react with 106 gms. of sodium carbonate, one assay-ton ore will react with  $106/60 \times 32.6$ , i.e., approximately 56 gms. of sodium carbonate.



$2 \times 223$  gms. 12 gms.

12 gms. of carbon will reduce 446 gms. of litharge and yield 414 gms. of lead. 1 gm. of carbon will yield 34.5 gms. of lead. As the reducing agent commonly employed is not pure carbon but wood-charcoal, its reducing power per gm. is only about 20 gms. of lead. A convenient weight of lead button to cupel being about 20-25 gms. of lead, the weight of charcoal to be used is one gram.

Alternative reducing agents are wheat-flour, argol, powdered coal or coke, sugar, etc.. Of these wheat-flour and argol are more in use than the others. The former has one-half, and the latter one-fourth, of the reducing power of charcoal. Argol is impure potassium hydrogen tartrate and is obtained as a sediment in the vats in which grape-juice is allowed to ferment. It owes its reducing power to carbon and carbon monoxide which result from its decomposition on heating. The reaction is represented as follows :—



The reducing power expressed in grams of lead per gram of reducing agent is ascertained by using the following charges :—Mix 60 gms. of litharge, 5 gms. of silica (quartz powder), 10 gms. of sodium carbonate and 1 gm. of charcoal on a sheet of glazed paper and charge into a fire-clay crucible, using size 'D' crucible.

Give it a cover of about 5 gms. of borax glass. Mix and charge into each of two more 'D' size crucibles a similar charge to the above but using 2 gms. of wheat flour in one and 4 gms. of argol in the other, in place of 1 gm of charcoal. Melt the charges by placing the crucibles in a wind-furnace. When the charges have melted and the fusion is quiet, i. e., when no gas bubbles are issuing from the charge, remove from the furnace and pour into separate moulds the contents of each of the three crucibles. Allow to cool. Detach the button of lead from the slag by hammering this off and weigh. Divide the weight of lead obtained in each case by the weight of the respective reducing agent to obtain the reducing power.

It may be pointed out here that the omission of silica from the above charges will not make any difference in the reducing power of the substances considered. That is to say, whether the charge is basic, neutral or acidic, the reducing power is always the same. The case is different as will be seen later, when the reducing power of sulphide minerals is to be determined. The basic or acid nature of the charge has a considerable influence on their reducing power.

The fire-clay crucibles\* used in fire-assay work are known as 'Battersea Rounds', the term having reference to the place of manufacture namely, Battersea, England, and to the shape, of these crucibles. The sizes are designated by the letters of the English alphabet. Size 'A', having a top diameter of  $1\frac{5}{8}$ " and a height of  $2\frac{5}{8}$ ", is the smallest. There is a progressive increase in the

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\* To be had from the Kumardhubi Fire-clay and Silica Works, Ltd., Kumardhubi (Manbhum.)

Fire-clay crucibles made in the Dept. of Ceramics of this University have been found to give fair service.

diameter, of about  $\frac{1}{4}$ " , and, in the height, of about  $\frac{1}{2}$ " , as one passes from size 'A' to size 'N' which is the largest. The crucible size should be selected for the work on hand with due regard to the fact that the charge will not be blown over due to the escape of the gas, mainly carbon-di-oxide, during melting. The most convenient sizes to employ for the various operations are shown in the following table :—

Nature of Experiment	Size	Height	Diameter	Approx. volume in ml.
Reducing power of charcoal, argol, etc. }	C	3 $\frac{1}{2}$ inch	2 $\frac{1}{4}$ inch	70
do D	D	4 „	2 $\frac{3}{8}$ „	100
Fusion of the charge for a straight ore }	F	5 „	3 „	175
do		5 $\frac{5}{8}$ „	3 $\frac{3}{8}$ „	340

A crucible is not to be discarded after using it once. It should be used until it becomes unserviceable on account of cracks. It is cleaned for use by melting a charge of 10-20 gms. of sodium carbonate, 40 gms of litharge and 1 gm. of charcoal and pouring out the charge after the molten mass is tranquil. This process will remove any adhering slag containing 'values', arising out of improper manipulation during the previous working of a charge.

Not only are crucibles to be selected with regard to the volume of the charge on hand but cupels also should be selected with regard to the size of the lead button to be cupelled. As already mentioned, a cupel will absorb a weight of lead monoxide roughly equal to its own weight.

The sizes of cupels are indicated by the numbers 1, 2, 3, 4, etc., number 1 size being the smallest, when they are made of bone-ash. When made from burnt magnesite, they are designated by the letters of the

alphabet, size 'A' being the smallest. Considering cupels of the same size, the latter variety has a much higher absorptive power for lead monoxide than the former. This variety is known as 'Morganite'. The variety known as 'Mabor' is probably made from mixture of bone-ash, portland cement and burnt magnesite.

Cupels can be made from bone-ash using a cupel mould. It is admixed with water, the quantity being so adjusted that the moistened material when pressed in the hand does not adhere to it. Cupels must be made at least six months prior to use. They must be dried slowly.

Brand	Size 'Number' or 'letter'	Diameter at top	Absorptive capacity
Morganite	B	$\frac{7}{8}$ inch	5 gms.
"	C	1 "	$7\frac{1}{2}$ "
"	F	$1\frac{3}{8}$ "	20 "
"	G	$1\frac{1}{2}$ "	30 "
Mabor	5	$1\frac{1}{2}$ "	18 "
"	6	$1\frac{13}{16}$ "	24 "
Bone-ash	1	$\frac{3}{4}$ "	3 "
"	6	$1\frac{3}{8}$ "	20 "
"	7	$1\frac{1}{2}$ "	28 "

Bone-ash varies in composition according as it is derived from the bones of ox, sheep, etc. . The following is the approximate composition of a sample of bone-ash :—

Calcium phosphate	84-85%
Calcium carbonate	9-10%
Calcium fluoride	3-4%
Magnesium phosphate	1-2%

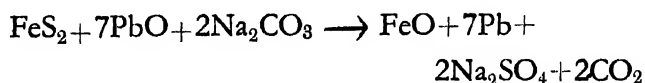
The addition of  $\frac{1}{2}$  A. T. of borax glass is made to a crucible charge to make the slag thin and to combine with any iron, copper, manganese, nickel, cobalt and manganese that may be present in the ore. Borax glass is obtained by heating the commercial variety of borax to a temperature which is about  $50^{\circ}\text{C}$ . higher than its melting point in a fire-clay crucible and pouring the melt on to a clean copper tray. It is then broken up into lumps and stocked for use. On heating, the commercial borax loses its water of hydration. The advantage of using borax glass over borax lies in the fact that a charge for fusion may be heated up rapidly without fear of mechanical loss of particles of the charge, due to the escape of steam, which follows the use of ordinary borax.

(3) In the case of arsenical ores, a preliminary roasting of one assay-ton of ore with 15 gms. of clean sand in a scorifier is necessary. Otherwise, the slag formed will carry some gold and silver. The roasting expels the arsenic as  $\text{As}_2\text{O}_3$  and converts S to  $\text{SO}_2$ , which also passes off. The sand added keeps the mass porous and thereby helps the expulsion of  $\text{As}_2\text{O}_3$ . The roasted ore is then fused in a crucible, the charge being the same as that for a quartz ore given above, except that an extra amount of sodium carbonate is necessary to flux off the sand, which was added to prevent fusing of the mass during roasting.

(4) When iron pyrites is present in amounts exceeding 8% in the ore, a preliminary roast is necessary. The roasting removes S as  $\text{SO}_2$  and iron is left behind as  $\text{Fe}_2\text{O}_3$ . In the subsequent fusion, if an extra amount of charcoal is introduced,  $\text{Fe}_2\text{O}_3$  will be reduced to  $\text{FeO}$ , which then combines with  $\text{SiO}_2$  in the ore forming  $\text{FeSiO}_3$ . The charge for fusion will be the same as for a quartz ore, only a little more charcoal will have to



be provided to reduce  $\text{Fe}_2\text{O}_3$  to  $\text{FeO}$ . Fusion without roast will involve the employment of so large a weight of  $\text{PbO}$  that the lead button will be very heavy. Also the excess of  $\text{PbO}$  will attack the crucible. The reactions taking place when iron pyrites are present and when the crucible fusion is adopted without a preliminary roast are:—

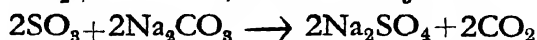
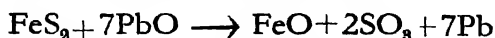


From this, it is clear that the lead button obtained will be very large. Large size cupels will be required for cupelling large size lead buttons and the volatilisation losses of precious metals will be high in such cases. Hence it is advantageous to roast preliminary to fusion when the usual quantity of  $\text{PbO}$  will suffice.

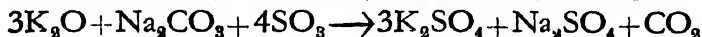
As an alternative to roasting, highly pyritic ores may be subjected to an oxidising fusion. The oxidant employed is potassium nitrate, commonly known as nitre, and is introduced into the crucible charge. The introduction of this has the effect of reducing the weight of lead button, thereby reducing the time of cupellation and thus minimising the volatilisation losses. The quantity of nitre to be introduced in a charge depends on the nature of the ore, whether highly pyritic or only some-what so, whether the associated metals are copper, antimony, lead, etc. besides iron. The example worked out below in full on the assumption that the associated metal is iron, is illustrative of the method of calculation :—

Suppose the sulphur content of the ore is 20%. If one A.T. of the ore is to be used for the assay, the sulphur contained in this will be 6.5 gms. This will be associated with 5.6 gms. of iron, making a total of

12.1 gms. of iron pyrites. The oxidation of this can be effected by 157 gms. of lead monoxide as can be seen from the following equations:—



The weight of lead button that would result from this is about 148 gms. As such a lead button will cause a high volatilisation loss during cupellation, lead monoxide is seldom used exclusively. The objection to the exclusive use of nitre for oxidation lies in the fact that it does not provide a means for collecting the precious metals. The following equations represent the oxidation by means of nitre:—



The oxidation of 12.1 gms. of iron pyrites will require 30 gms. of nitre. But for the reason already given, this is never used as the sole oxidant. Both lead monoxide and nitre are introduced as oxidants. The quantity of each entering into the charge is based on the fact that about 20 gms. of lead must be provided for alloying with the gold and the silver present in the ore. This will result from the use of 22 gms. of lead monoxide. This weight will oxidise 1.7 gms. of iron pyrites, leaving 10.4 (12.1—1.7) gms. for oxidation by nitre. This will require  $\frac{30}{1.7} \times 10.4$  or 26 gms. of nitre to the charge and the addition will have the effect of reducing the weight of lead button from 141 gms. to 20 gms. The power of nitre per gram to 'keep back' or to decrease the weight of lead button, which will otherwise result, is  $\frac{148-20}{26} = \frac{128}{26} = 4.6$  gms. This example has been worked out on the basis of a knowledge of

the composition of the ore, at least so far as the sulphur content is concerned. But such a knowledge is not necessary. A preliminary assay using charges described below will enable one to decide on the final charge. Charges based on rule-of-thumb method as to the ability of nitre to decrease the weight of lead button yield sometimes no lead button at all, though a mixture of lead monoxide and nitre is introduced into the charge. This is because the entire oxidation of the sulphide minerals is thrown on nitre. Such cases point to the importance of carrying out preliminary experiments before making up a final charge.

Determine the oxidising power of nitre as follows :—

( a ) Introduce into a 'C' size crucible a mixture of 60 gms. of granulated lead, 3 gms. nitre and 1 gm. silica. Heat in a wind furnace until thoroughly melted. Pour the melt into an iron mould. Allow to cool. Hammer off the slag and weigh the button of lead. The difference between the weight of lead originally taken and that of the button obtained, divided by 3 gives the oxidising power of nitre per gram. The theoretical value is 15 gms. lead per gram nitre.

( b ) Introduce into a second crucible of the same size as in ( a ) the following charge, after thoroughly mixing on a sheet of glazed paper :—

Charcoal ( the same charcoal as was used to 1 gm.  
determine the reducing power of charcoal )

Lead monoxide 85 gms.

Nitre 3 gms.

Lead monoxide ( as cover ). 5 gms.

Fuse in a wind furnace, pour the melt when tranquil into a mould, remove the solidified mass from the mould, hammer off the slag and weigh the lead. Supposing the reducing power of charcoal to be 18.6 gms. and the weight of lead button obtained in this

case to be 7.4 gms, the difference is 11.2 gms. On account of the introduction of 3 gms. of nitre, the weight of lead button has been reduced by 11.2 gms. Hence, 1 gm. nitre will keep back 3.7 gms. lead. In other words, it decreases the weight of lead button by 3.7 gms. per gm. nitre employed.

It is this value that is of more immediate application to the cases that arise in practice than the value obtained in ( a ). The value obtained depends on whether the oxidation is carried out under conditions where the charge is basic or acidic. Under the former condition, the value is about 4.8 gms. whereas under the latter condition, it is about 4.0. These values are only approximate and are not of universal application. Each specimen of ore is to be investigated by preliminary runs before deciding on the weight of nitre to be added.

The following charges are suggested for the trial runs :—

	A	B
Pyritous ore	5 gms.	5 gms.
Silica	8 „	8 „
Litharge ( Lead monoxide ) }	100 „	100 „
Soda-ash (sodium carbonate) }	12 „	12 „
Borax glass	5-8 „	5-8 „
Nitre	Nil	3 gms.

The difference in the weights of lead button obtained in the two cases divided by 3 gives the number of gms. of lead by which the weight of lead button can be decreased per gram addition of nitre.

( 5 ) In the case of ores, concentrates, etc. containing high percentages of copper, difficulty is experienced in cupellation when they have been fused with the usual quantities of fluxing reagents. The copper is not

eliminated completely during cupelling unless a very large amount of lead, i. e., sixteen times the weight of copper present, is employed and with a large weight of lead button, the time of cupelling is prolonged, leading to high volatilisation losses. To obviate this difficulty either pot fusion followed by scorification and cupellation or a combination of wet and dry methods is used.

The following charges are recommended for the above classes of ores and metallurgical products when pot i. e., crucible fusion is followed by scorification and cupellation :—

Constituents of the charge	Ore Weight	Concentrate Weight	Matte Weight
Ore, concentrate or other product	1/2 A. T.	1/2 A. T.	1/8 A. T.
Lead monoxide	65 gms.	65 gms.	30 gms.
Sodium carbonate	25 gms.	25 „	25 „
Nitre	8 gms.	8 „	
Borax	20 gms.	20 „	10 „
Silica	5 gms.	5 „	1 „
Charcoal			0.8 „

Copper and silver in an ore are dissolved in  $\text{HNO}_3$ , Ag precipitated as AgCl by means of conc. HCl, the excess HCl removed by the addition of  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  when  $\text{PbCl}_2$  is thrown down as a precipitate carrying with it the particles of gold, the liquid filtered off, and the residue fused with an ordinary charge followed by the usual operations.

### The Scorification Assay :—

As an alternative to the combination assay, mentioned above, an assay known as the 'Scorification Assay' is employed for this class of ore, especially when it is rich in gold (i.e.) 2 oz. or more to the ton. The assay is based on the fact that when such ore is roasted in a fire clay

dish known as a 'scorifier' mixed with a large weight of granulated lead and a little borax, a slag consisting of lead silicate and copper borate is obtained, the precious metals forming an alloy with lead. The melt is poured into a mould, the slag hammered out when cold, and the alloy cupelled and parted in the usual manner.

Details of working the two processes are as given below :—

**'Combination' or 'Wet and Dry' Assay :—** Heat 1 A.T. of ore with 100 ml.  $\text{HNO}_3$  in a 400 ml. beaker, cover with a watch glass, and heat for 1 hour. Cool, dilute with 100 ml. water, add 1 ml. conc.  $\text{HCl}$ , stir well, add 20 ml. of 10% lead acetate solution. Shake and let stand. Decant through a filter-paper. Wash two or three times by decantation. Dry the residue in the beaker and add the filter-paper with the small amount of residue to the beaker. Transfer to a fire-clay crucible and charge into it litharge, sodium carbonate, charcoal, and borax in quantities usual for a quartz ore. Carry out the fusion, cupellation and parting operations in the usual manner.

### **The Scorification Assay Procedure :—**

Mix  $\frac{1}{2}$  A. T. ore with 25 grams of grain lead. Introduce into a scorifier. Cover it with 25 gms. of grain lead and 1–2 gms. borax. Introduce into a muffle. Close the door of the muffle. Gradually raise the temperature to a red heat so that the charge melts completely. Open the door of the muffle. The lead oxidises and forms a silicate with the silica of the ore. This collects all round the edge of the metallic layer leaving a bright central spot known as the 'eye'. As more and more lead silicate forms, the 'eye' gets smaller and smaller until when all the silica has combined with the lead oxide, the 'eye' closes due

to the slag covering the metal completely. Pour the contents of the scorifier into a mould. When cold, detach the solidified mass from the mould, hammer out the slag, separate the lead button and cupel and part in the usual manner.

The scorification is often used as an adjunct to the crucible fusion when a very large lead button is obtained as in pyritous ores, which have not been roasted prior to fusion. It is neither accurate nor profitable to cupel directly heavy buttons. Scorification of a heavy lead button yields a convenient weight of lead button to cupel. It also eliminates Cu as copper borate.

(6) In the case of ores containing stibnite, the combination assay may be adopted with advantage in place of an oxidising fusion with nitre. When antimony enters the gold-silver-lead button, it leads to the bursting of the cupell during the cupellation due to the formation of antimoniate of lead.

Procedure for the combination assay for antimonial ores :—

Dissolve 1 A.T. ore in 100 ml. conc. HCl in a 400 ml. beaker by heating for about half to one hour. Add 3–4 gms. tartaric acid. Dilute with 100 ml. water. Shake well. Filter by decantation. Wash two or three times with water, decanting off the solution. Dry the residue in the beaker by heating on the hot plate. Transfer the residue to a fire-clay crucible with the usual fluxes in quantities mentioned for a straight quartz ore, fuse, cupel the lead button and part as usual.

(7) **Telluride Ores** :— These require very fine grinding. No roasting is necessary as a preliminary to the ordinary crucible fusion. It is highly important that the temperature of fusion should be gradually raised. To prevent tellurium from passing into the metal from

the slag, a very large amount of  $\text{PbO}$  ( 5 times the weight of ore ) is necessary.

The following is a typical charge :—

Ore	1 A. T.	$\text{Na}_2\text{CO}_3$	1 A. T.
$\text{PbO}$	5 „	Borax	10-12 gms.
		Salt	as cover.

(8) Sometimes it is necessary to determine the amount of gold taken up by cupels.

The following is a typical charge for the purpose :—

Cupel (crushed fine)	1 A. T.
$\text{Na}_2\text{CO}_3$ (anhydrous)	20 gms.
Borax glass	8 „
Fluorspar	30 „
Charcoal	1.5 „
Litharge	2-3 „

Pure gold and pure silver for '*check*' assay are prepared in the manner shown in Experiment 54 A.

Sometimes it happens that an ore does not pass through a 60 mesh sieve completely. The particles of metal thus retained on the sieve during the final stage of grinding preparatory for weighing out a charge are referred to as '*metallics*'. These are rich, having an assay-value 5-20 times the value of the portion passing through the sieve. To get the gold content of the entire mass of ore, the two portions are assayed separately. The -60 portion ( i.e., that passing through the sieve ) is assayed by the pot ( i.e., the crucible ) fusion method, followed by cupellation and parting. The +60 portion is assayed by a method which depends upon its quantity. If small in quantity, the portion may be dissolved in aqua regia and the solution made up to a definite volume. Of this a measured volume, bearing a definite ratio to the charge for fusion of the -60 portion is added to it and the usual operations performed.



The following examples illustrate the method of calculation :—

**Example 1** :—A sample of ore weighing 150 gms. leaves 19.4 gms. of 'metallics' on a 60 mesh sieve. The --60 portion and the + 60 portion assay 1 oz. 10 dwts. and 7 ozs. of gold per ton respectively, by the crucible assay. The assay value of the entire ore is :—

1 A.T. of—60 ore yields 1.5 mgms. gold  
 (150-19.4) or 130.6 gms. or  $\frac{130.6}{32.66}$  A. T. yield  $1.5 \times 4$   
 mgms. gold.

1 A.T. of + 60 ore yields  $\frac{6 \text{ mgms. gold,}}{7 \text{ mgms.}}$

$\frac{19.4}{32.66}$  A.T. of + 60 ore yields  $\frac{7 \times 19.4}{32.66}$  mgms.

= 4.15 mgms.

Gold in  $\frac{150}{32.66}$  A.T. ore = 10.15 mgms.

„ 1 A.T. =  $\frac{10.15 \times 32.66}{150}$

= 2.21 mgms.

1 ton of 2240 lbs. of the ore assays 2 ozs. 4 dwts. and 5 grains.

**Example 2** :—A sample of ore weighing 150 gms. leaves 2.04 gms. of 'metallics' on a 60 mesh sieve. The entire 'metallics' portion is dissolved in aqua regia and the solution made to 5 ml. . 1 A.T. of the—60 ore is charged into a crucible with the usual fluxes and 1.1 ml. of the solution of the 'metallics' is added to the charge by a pipette graduated in tenths of a ml. and the usual operations performed.

The number of mgms. of gold obtained is 2.

Hence, the ore contains 2 ozs. of gold per ton.

From the following it will be clear why 1.1 ml. of the aqua regia solution is added to the charge in the crucible.

147.96 gms. of—60 portion are associated with 2.04 gms. 'metallics'

$$32.66 \quad , \quad , \quad , \quad \frac{2.04}{147.96} \times 32.6 \quad ,$$

2.04 gms. are contained in 5 ml.

$$\frac{2.04 \times 32.66}{147.96} \text{ gms. } , \quad , \quad \frac{5}{2.04} \times \frac{2.04 \times 32.66}{147.96} \\ = 1.1 \text{ ml.}$$

### Precaution to be taken in the operation of cupelling.

The floor of the muffle is rapidly corroded by any lead monoxide that may be spilt accidentally. To guard against such corrosion, a layer of bone-ash  $\frac{1}{4}$ " thick must be spread on it evenly before lighting the furnace.

Testing the Reagents used in Fire-Assay for Ag.:—  
Litharge PbO Melting point  $877^{\circ}\text{C}$ . This may contain some silver. The amount of silver present is determined once for all in a lot of the material, using one of the following charges :—

Charge I		Charge II
Litharge 120 gms.	PbO	90 gms.
Sodium bicarbonate 60 gms.	$\text{Na}_2\text{CO}_3$	20 "
Argol (potassium	Silica	7 "
hydrogen tartrate ) 2 gms.	Borax }	5 "
	glass }	"
	Argol	2 "

The constituents are mixed thoroughly upon a sheet of glazed paper and the mixture placed in a fireclay crucible ( size F ) and covered with a layer of finely powdered dry common salt. The crucible is placed in a wind furnace. When the charge has reached the

state of quiet fusion, the crucible is with drawn from the furnace, slightly tapped upon its bottom and on its side and poured into a mould. When cold, the slag is hammered off from the button of metal. This is cupelled and the button of silver which results is weighed. In subsequent work with this lot of litharge, a deduction for Ag equal to that obtained on the weight of PbO employed is made.

### EXPERIMENT 54-A

#### **Determination of the Fineness of 'Gold' of a piece from a Watch-chain**

By the term 'fineness of gold' is meant the number of parts of gold per 1000 parts of an alloy.

#### **Principle —**

When an alloy of gold and silver containing less than 30 parts of gold and more than 70 parts of silver per 100 parts of the alloy is treated with nitric acid, the latter goes into solution while the former is left behind unaffected. After decanting the solution and washing the residue with water, it is heated, cooled and weighed in an accurate balance. The 'fineness' is calculated from the original weight of the alloy and the final weight of the pure gold.

The yellow colour of the piece to be examined is an indication that the alloy contains more than 30 parts of gold. As 'parting', that is, separation of the gold from the silver, can be effected only when the alloy contains 30 parts or less of gold, the content of gold must first be brought down approximately to 30 parts by adding pure silver to it, wrapping the two in a piece of pure lead foil and melting the whole in a cupel in a muffle furnace. During the process the oxide of lead is absorbed by the cupel, the alloy of gold and silver being left

behind. The cupel is cooled, the button is removed, hammered, annealed and parted with nitric acid.

### Procedure :—

Weigh accurately a piece, say 0.6000 gm. Wrap this up with 1.5 gms. of pure silver in pure lead sheet weighing about 4 gms. and introduce by means of assay tongs into a hot cupel placed in a muffle furnace. When the surface of the molten alloy in the cupel appears bright, withdraw the cupel from the furnace. Hammer the cold button of metal on an anvil to a thin foil 5 cms. long and  $\frac{1}{2}$  to 1 cm. broad. Roll into a prill after *annealing*, (i.e.,) raising to a red heat in the Bunsen burner flame. Heat a mixture of 10 ml. conc.  $\text{HNO}_3$  with 20 ml. of water in a wide mouthed test tube or in a parting flask. Introduce the prill into the hot boiling acid. Boil for 10 minutes. Decant the solution. Add a little more of the acid mixture, heat to boiling and then decant. Wash with water five or six times. Fill the tube or the parting flask with water finally, cover the mouth of the same with a crucible and invert the whole quickly. The gold is transferred to the crucible by this means. Decant off the water. Drain the water to the last drop. Dry. Heat to dull redness. Cool. Transfer to one of the pans of the bullion balance and weigh.

### Example :—

Weight of the piece from the chain	0.6642 gm.
Weight of silver added	1.5 gm.
Weight of lead sheet	4.0 gm.
Weight of gold after parting	0.58260 gm.
Fineness of gold is . . .	$0.58260 \times 1000 / 0.6642$
	i. e. 877

When expressed in carats the result is  $24 \times 877 \div 1000$ , i. e., 21.05. Gold which is 1000 'fine' is referred to as 24 carat gold.

## NOTES :—

(1) The process of enriching the alloy in silver so as to make a satisfactory separation of the gold, from the silver, possible, is known as inquartation. This term has arisen from the fact that gold in the alloy must be a quarter or one fourth part of the whole in order that parting with  $\text{HNO}_3$  may be effected.

(2) As the absorption of gold by the cupel becomes perceptible when a large amount of lead is employed for the cupellation, the weight of it must be limited to the minimum needed for effecting a removal of other base metals. When the fineness of gold and silver is 800-900, E.A. Smith recommends 6 gms. of lead for 0.5 gm. of the alloy.

(3) Though parting can be effected with alloys containing 95 parts silver to 5 parts gold, it is convenient to make such an addition of silver to the alloy as will bring up the % of silver to 70. Such an alloy does not yield gold in a *finely divided condition on parting* and therefore there is no fear of loss of particles during decanting, washing and transferring to the crucible.

(4) Allowance must be made for the losses during cupellation. This is done as follows :—Weigh 0.58260 gm. pure gold into a cupel, add 1.5 gms. silver and wrap in 2 gms. of lead sheet. Cupel. Part. Weigh the resulting gold. Suppose the weight is 0.5831 gm. The gain is 0.0005 gm. Then, this gain will also have occurred in the sample assayed. Hence .0005 gm. known as 'surcharge' must be subtracted from the weight of gold obtained on the sample assayed. In the example under consideration, the corrected weight of gold will be .5821 gm. . The 'check' run and the 'assay' run must be made under the same conditions. At the mint, the general practice is to

run a preliminary assay on the sample which enables one to decide on the weight of pure gold to be taken for the 'proof' or the 'check' run and also the weights of silver and lead to be added to the charge. The 'proof' and the sample runs are made side by side in the same muffle. The second run so made on the sample is referred to as the 'final assay'. The latter may yield results 10 parts or more per 1000 higher than the preliminary assay.

(5) The procedure for the assay of a gold coin, the sovereign for instance, current in our country, or of gold bullion, does not differ from the one outlined above. The following data will be useful in determining the charge for the assay and the 'proof' or 'check':—

Fineness of gold in the sovereign = 916.6 per 1000.

By difference, parts of Cu = 83.4 „ „

Fineness of coin or bullion.	Wt. of coin or bullion	Wt. of lead
950-1000	0.5 gm.	2 gm.
900-950	„	4 „
800-900	„	6 „

For every 100 parts below 800 add at the rate of 4 gms. lead. On account of the low solubility of copper oxide in lead monoxide, elimination of the former is possible by employing about 100-200 times as large a quantity of lead as copper. The standard weight of a sovereign is 123.27447 grains and no sovereign is put into circulation which is 0.17 grain heavier or lighter than the standard. When a coin has lost 3 grains, it is withdrawn from circulation. The approximate loss of weight in one year is 0.029 grain. The following are representative assays of the mill and the cyanide bullions :—

	Gold	Silver
	Parts per 1000	Parts per 1000

The mill bullion from the amalgamation plant	926.11	66.12
The cyanide bullion from the residues from zinc treatment.	895.85	87.31

The parts of silver in a gold bullion are obtained as follows:—

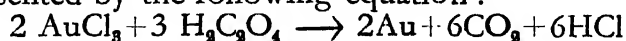
Determine the parts of gold as outlined above. Determine the weight of gold and silver together on a sample which is cupelled without the addition of silver, the weight of bullion taken being the same as for the determination of the gold content. The weight of pure gold subtracted from the weight of gold plus silver button gives the weight of silver. Express in parts per 1000.

(6) Pure gold and silver required in these assays are made as follows:—

**Pure gold** :—Weigh 5 gms. of the purest gold available into a 400 ml. beaker. Add a mixture of 10 ml. conc.  $\text{HNO}_3$  and 30 ml. conc.  $\text{HCl}$ . Heat in a water bath. Bring to low bulk with the addition of  $\text{HCl}$  by heating for a prolonged time on the water bath. Pour the contents into a litre beaker containing about 800 ml. distilled water. Allow the precipitated  $\text{AgCl}$  to settle undisturbed for a week. Siphon off the clear solution of  $\text{AuCl}_3$  into a second beaker. Warm to  $60^\circ\text{C}$ . Introduce crystals of oxalic acid and stir well. Allow to stand for a day or two. Wash by decantation. Filter through a filter paper, give one or two washes with ammonia water to remove the last traces of silver chloride, wash several times with water. Melt in a clean crucible. Pour into an iron mould. Hammer on an anvil to a thin plate. Immerse in  $\text{HCl}$ . Wash with water. Preserve in a bottle for use after heating to dull redness and cooling.

**Pure silver :—**Dissolve of 12 gms. of silver bullion in 100 ml. 1:1  $\text{HNO}_3$  in a beaker with the aid of gentle heat. Dilute with water. Allow to settle any gold particles present, siphon off the clear liquid. Add to the siphoned liquid dil.  $\text{HCl}$  in excess. Stir vigorously. Allow the precipitate to settle. Decant off the clear liquid. Repeat the process several times until the decanted liquid is free from  $\text{HCl}$ . Dry by heating in the air oven. Transfer to a glazed paper. Mix with twice its weight ( 30 gms ) of anhydrous sodium carbonate and fuse in a clean clay crucible. Cast into an iron mould. Hammer out the slag, clean the ingot by washing with hot water and beat on the anvil to a thin sheet.

The reduction of auric chloride to metallic gold is represented by the following equation :—



#### EXPERIMENT 54-B.

#### Silver in a Silver Coin.

The cupellation process described in Experiment 54-A for the assay of a piece of watch-chain made of gold is available for the determination of silver in the rupee coin current before the introduction of rupee coins of nickel. As described thereunder, a preliminary assay will have to be made first and on the basis of this, a check assay is made with an alloy of pure silver and pure copper mixed in the proportions in which they are present in the coin alongside of the final assay. But a shorter and less elaborate method due to Gay-Lussac is generally practised at the mints.

When a standard solution of sodium chloride is added to a solution of the coin in  $\text{HNO}_3$ , silver chloride is precipitated. The point at which the addition of sodium chloride is to be stopped is indicated by the absence of a cloudiness at the contact surface of the two solutions.



**Solutions Required :—**

1. Sodium chloride solution :— Dissolve 5.4162 gms NaCl in 1 litre of water. 1 ml. of this = 0.01 gm. Ag.

2. Decimal salt solution : Dilute 100 ml. of solution No. 1 to 1000 ml. exactly in a litre measuring flask. 1 ml. of this soln. = 0.001 gm. Ag

3. Standard Silver Nitrate Solution :— Dissolve 1 gm. pure silver in 20 ml. dil.  $\text{HNO}_3$  (s.g. 1.2) and dilute to 1 litre.

1 ml. of this = 0.001 gm. Ag

**Procedure for Standardisation :—**

Weigh out 1.05 gm. pure silver exactly. Dissolve in 10 ml. dil.  $\text{HNO}_3$  (s.g. 1.2) in a 200-250 ml. capacity bottle from which the stopper is removed. Blow out nitrous fumes. Add from a pipette or a burette 100 ml. of solution No 1. Shake well after putting the stopper in place. Let stand until clear. Run in solution No. 2, 1 ml. at a time. See if there is any cloudiness at the junction. If there is, shake until clear. Continue adding until no cloudiness is seen. The amount of solution No. 2 used is 54 ml. This is equal to 5.4 ml. of solution No 1. Hence, the amount of solution No. 1 used in all will be 105.4 ml.

105.4 ml. NaCl = 1.05 gm. Ag.

1 ml. , -  $\frac{1.05}{105.4}$  gm. Ag. = 0.009963 gm. Ag

**NOTE:—**

The addition of solution No. 2 does not produce any cloudiness when the weight of silver is less than 1 gm. In that case add 5-10 ml. of solution No. 3, so that a cloudiness appears on adding solution No. 2. Add this until no cloudiness is produced. The amount of silver in solution in this case will be the weight of silver taken plus the equivalent in silver of the volume of solution No. 3 which was added.

## EXPERIMENT 55.

**Determination of Platinum in Platinum Alloys.**

Alloys of gold and platinum are used in jewellery and dentistry. The colour of these alloys gives an indication of the extent to which platinum may be present. Up to 15% platinum in the alloy, the colour is yellow. Alloys containing 25% platinum and more are distinctly white.

**Principle of the Assay :—**

This is the same as for gold bullion or gold coin. The alloy is wrapped in lead foil along with silver and cupelled, the cupelled button parted and the resulting button of gold and platinum weighed. This is then dissolved in aqua regia. The solution which is a mixture of gold chloride and chloroplatinic acid is evaporated to low bulk twice with hydrochloric acid to eliminate nitric acid. Gold is then precipitated from the solution by means of oxalic acid. This is filtered off and weighed. By difference, the weight of platinum is obtained. Alternatively, the filtrate from the gold residue is evaporated to dryness and heated strongly until no more fumes come off. The residue is platinum and is directly weighed.

**Procedure :—**

Weigh 0.5000 gm. of the alloy and wrap it in 12 gms. of lead foil and 1.5 gms. silver. Introduce into a hot cupel. Carry out the cupellation at a temperature about 50°-100°C higher than for the assay of a gold bullion. When all the lead monoxide has been absorbed by the cupel, withdraw it from the muffle and detach the button when cold. Part the button with nitric acid. Wash the residue, dry, anneal and weigh. Dissolve

the same in 20 ml. of aqua regia in a 100 ml. beaker. Evaporate on a water bath to about 4 ml. Add 20 ml. of hydrochloric acid, evaporate to low bulk and repeat the evaporation to low bulk with hydrochloric acid a second time. Dilute to 20 ml. with water. Add a gram or two of oxalic acid and heat to boiling. Dilute with water to 50 ml. Let settle. Filter using a 5 or 7 cm. filter paper receiving the filtrate in a platinum basin. Wash residue 3 or 4 times with water. Ignite the paper and weigh the gold. Evaporate the contents of the platinum basin to dryness. Heat strongly until no more fumes are evolved. Weigh. By difference calculate the weight of platinum.

NOTES :—

(1) Parting with nitric acid is satisfactory only if 1 to 2 parts of platinum are present in 1000 parts of the alloy. On the basis of the results of a preliminary assay, the final assay can be carried out correctly, employing silver for alloying so that the cupelled button has 1-2 parts of platinum per 1000 of the alloy.

(2) Parting with concentrated sulphuric acid in a silica or platinum vessel after an inquartation with silver may be substituted. Bumping effect is reduced by the introduction of glass capillary tubes. Several hours' heating will be necessary to dissolve out the silver. Decant. Wash with water several times. Dry, heat and weigh the residue of gold and platinum. Dissolve in aqua regia, complete the precipitation of gold with oxalic acid. Filter, evaporate and heat to complete expulsion of fumes, cool and weigh the platinum. Parting with sulphuric acid is more satisfactory with alloys rich in silver and platinum.

## EXPERIMENT 55 A.

**Control Tests in a Gold Mine.****a. Assay of 'Headings' and 'Tailings'.**

'Headings' is the term applied to the cyanide solution entering the 'zinc boxes' wherein the gold is precipitated by means of zinc and 'tailings' is the term applied to the liquid leaving the 'zinc boxes'. To exercise control on the efficiency of recovery of gold in these boxes, it is of the utmost importance to determine the gold contents of the 'headings' and the 'tailings'. As in the case of the analysis of gold ore, the results are expressed in ozs. per ton of each of the solutions.

The weights of the solutions to be taken for an assay are largely governed by their gold contents which for the 'headings' and the 'tailings' are in normal practice 15-40 grains and 0.2-0.4 grain per ton respectively. The weight of the solution taken is 10,800 grains. This is approximately 22 A. T.

**Principle :—**

When the solution is treated with zinc, in the form of dust or shavings, and a solution of lead acetate, a zinc-lead couple is formed which displaces gold from the solution. The gold set free is collected by the particles of spongy lead remaining in the medium when the zinc is dissolved by the subsequent addition of hydrochloric acid. The lead containing the gold is filtered off, cupelled, and parted in the usual manner.

**Procedure :—**

Into a 1600 ml. beaker weigh out 10,800 grains of the cyanide solution. Add 300 grains of lead acetate.

Bring to a boil. Add 100 grains of zinc shavings. Keep at a boiling heat for about 1/2 hr. Add 65-70 ml. commercial conc. HCl and continue boiling for 10-15

minutes longer. Lead, silver and gold collect into a mass, while the zinc passes into solution as  $\text{ZnCl}_2$ . Dilute with cold water, let stand and decant through a lead filter cone, fitted to a funnel. The cone is made from sheet lead. It has a number of holes pricked in and about its apex.

Repeat washing by decantation 3 or 4 times. Finally transfer the mass of lead with the gold and silver precipitated on it to the filter cone. Squeeze out the water by pressure from the flattened head of a glass rod. Dry the filter cone of lead with its contents. Transfer to a hot cupel.

Add 20-30 mgms. of silver. Place at the mouth of the muffle until the moisture is expelled completely. Push it into the hottest part and allow to remain there until the bead of metal brightens up. Withdraw the cupel from the furnace. Cool. Detach the button and weigh.

NOTE :—

This method is applicable to 'headings' and 'tailings' and is rapid.

### **b. Alternative Method**

**Principle :—**

When the cyanide solution is treated with  $\text{CuSO}_4$  and  $\text{Na}_2\text{SO}_3$  and acidified, gold and silver are precipitated and held by the cuprous cyanide which is also formed as a precipitate simultaneously. The coagulation of the entire precipitate is helped by the addition of potassium ferrocyanide. The precipitate is then filtered off, transferred to a fire-clay crucible, 2-3 ml. of 0.1-N  $\text{AgNO}_3$  solution added and fused with 2 A. T. of the following flux, the lead button separated from the slag, and the same then cupelled and parted in the usual manner :—

**Flux :—**

Sodium carbonate	270	gms.
Litharge	1000	„
Flour ( wheat )	40	„
Charcoal	25	„
Borax	150	„

**Procedure :—**

Weigh out 10,800 grains of the cyanide solution into a 1500 ml. beaker, add a few drops of a saturated solution of NaCN, then 20 ml. of each of the following solutions in the order given:—

- 20% copper sulphate
- 15% sodium sulphite
- 1.3 s.g sulphuric acid.
- 4% potassium ferrocyanide.

Stir well after each addition. Allow the solution to stand until  $\text{SO}_2$  gas is freely evolved. Filter through a large size fluted filter-paper. When thoroughly drained, dust a little of the above flux on the precipitate.

Introduce 1 A. T. of the same flux into a crucible. Then place the filter paper containing the precipitate on the mass of flux in the crucible, then finally add one A. T. more of the flux. Heat in a wind furnace, pour the metal and slag into a mould, hammer the slag off when cold and cupel button with the addition of pure silver. Part the bead and weigh.

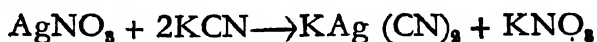
**NOTES :—**

This process has the disadvantage that it requires time and a number of solutions. But it is as accurate as the method first described.

### c. Determination of the % of KCN in a sample of cyanide.

#### Principle :—

When a standard solution of silver nitrate is added to a solution of the cyanide in water, a white precipitate forms which immediately dissolves in the excess of cyanide. This continues until the following reaction has taken place:—



Any addition of silver nitrate beyond this point is indicated by the formation of the yellow precipitate of silver iodide with potassium iodide introduced at the beginning of the titration.

#### Solutions Required :—

Standard  $\text{AgNO}_3$  soln. Dissolve 4.5333 gms in water and make up to 200 ml. exactly.

KI            2% solution.

#### Procedure :—

Dissolve 4 gms. of the cyanide sample in water. Make up to 250 ml. soln. the mark in a measuring flask. Mix well. Pour into a burette. Draw off 25 ml. of the cyanide solution from the burette into a beaker. Add 2 ml. of 2% KI solution. Allow 0.1-N  $\text{AgNO}_3$  to run from a burette until a yellow turbidity is produced. Repeat twice. Calculate the %KCN.

$$1 \text{ ml. } 0.1\text{-N } \text{AgNO}_3 = 0.013 \text{ gm. KCN}$$

#### NOTES :—

(1) Cyanide solutions are poisonous. Therefore measured volumes are run from a burette, *not pipetted off*.

(2) The method described above is applicable only to a sample of cyanide which is to serve as Stores material.

#### **d. Determination of the 'Total Cyanide' in the circulating cyanide solution in a mine :—**

**Introductory :—**An approximately 0.1% KCN solution is used for dissolving the gold from the pulp in the Tube mills. It is necessary to see that this strength is maintained in order that the gold may be dissolved. As the water from the mine is used in the mills and as the same is acid very often, the circulating cyanide solution is a complex mixture containing free hydrocyanic acid, zincocyanide, ferrocyanide, etc. .

#### **Principle :—**

The 'total cyanide' determination is based on the same principle as the one described in testing Stores material ; only, in this case, the free hydrocyanic acid is neutralised by the addition of NaOH before proceeding with titration.

**Solution and Indicators :—** Same as in Experiment 55 A-c.

#### **Procedure :—**

Measure out 130 ml. of the cyanide solution into a beaker. Add about  $\frac{1}{2}$  gm. NaOH, 2 ml. of KI and then 0.1-N  $\text{AgNO}_3$  from a burette until a yellow turbidity is seen.

#### **Record :—**

130 ml. required 10 ml. 0.1-N  $\text{AgNO}_3$ ,

100 ml. would require  $\frac{10}{130} \times 100$ ,

1 ml. 0.1 N  $\text{AgNO}_3$  = 0.013 gm. KCN.

100 ml. soln. contain  $\frac{10}{130} \times 100 \times 0.013$  gm.

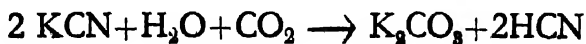
KCN i. e. 0.1 % KCN.



### e. 'Free Cyanide'

This is the term applied to KCN present as such in the solution ; the free hydrocyanic acid, formed as a result of decomposition by  $\text{CO}_2$  present in the air of the mine and in the mine water, not being included, as it is not capable of dissolving gold.

The decomposition is represented as follows :



Principle and procedure are the same as in the determination of 'Total Cyanide', except for the fact that the sodium hydroxide is omitted in this case.

## CHAPTER VII.

### EXPERIMENT 56.

#### Complete Analysis of Iron Ore

The determination of the chief constituent, namely Fe, has been described in Expts. 9 and 10. In deciding on the quantity of fluxing materials to be charged into an iron blast furnace it is necessary to know the complete analysis of an ore. The percentages of  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$  are particularly required for this purpose. A method for constituents not considered so far is described fully below while only references to the Experiments already described are given for the determination of those constituents previously considered.

##### Moisture :—

The ore is broken up to pea-size and 5-10 gms. weighed on to a cover glass, and heated in an air oven at  $105^\circ\text{C}$ ., to constant weight. The loss represents the moisture.

##### $\text{CO}_2$ :—

The ore is crushed fine to pass a 60-80 mesh sieve. Weigh 1 gm. into a porcelain crucible. Fit up the apparatus as shown in Fig. 19 a. Introduce 50 ml. dil.  $\text{H}_2\text{SO}_4$  of s.g. 1.2 into the flask. Loosely fill the tube T with anhydrous  $\text{CaCl}_2$ . Weigh the whole after introducing the crucible into the flask. Tilt so that the acid comes in contact with the ore. Warm for 10-20

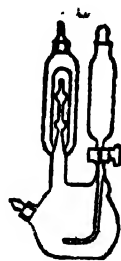


Fig. 19b

minutes. Cool and weigh. The loss in weight represents  $\text{CO}_2$ . An improved type of apparatus for this

determination is due to Schrotter and is shown in Fig 19 b. Dil HCl ( 1:1 ) fills the tap-funnel F and



Fig. 19 a

conc.  $\text{H}_2\text{SO}_4$  fills more than half of A. The use of this makes it possible to aspirate dry air through it at the end of an expt., thereby expelling  $\text{CO}_2$  that will otherwise remain in it. Greater accuracy results from its use.

### Ferrous oxide.—

Fit up the apparatus shown in Fig. 9, p. 125. This is used whenever any liquid is to be heated out of contact with air. An one-holed cork fits the mouth of the conical flask. A short piece of glass-tubing open at both ends passes through the hole in the cork and is either flush with the bottom of the cork or projects a little below it. A piece of rubber-tubing about 2" long and  $\frac{1}{8}$ " bore. fits into the free end of the glass tube. A glass rod is inserted into the free end of the rubber-tubing. A vertical slit  $\frac{1}{2}$  to  $\frac{3}{4}$  cm. long is cut in the middle of the rubber-tubing with a sharp pen-knife. Through this slit escape vapours and gases when the liquid in the flask is heated. It prevents the entry of air from outside into the flask. Introduce 1 gm. of the ore in the flask with a calcite piece. Add 20 ml. dil. HCl s.g. 1.1 Replace the cork with the valve attachment in position. Heat gently for 20 minutes. Cool. Dilute and titrate with  $\text{KMnO}_4$  as in Expt. 9 Calculate the % of  $\text{FeO}$ .

**$\text{Fe}_2\text{O}_3$  :—**

Obtain the total Fe as in Expt. 9. Subtract the Fe present as  $\text{FeO}$ . Calculate the difference as  $\text{Fe}_2\text{O}_3$ .

NOTE :—

The residue insoluble in  $\text{HCl}$  must be treated with  $\text{HF}$  and  $\text{H}_2\text{SO}_4$  and the product resulting from such treatment should be taken up with  $\text{HCl}$  and the solution added to the main solution and the determination of total iron then made.

**$\text{Al}_2\text{O}_3$  :—**

**Case 1.** The ore is free from titanium. Test for titanium in an ore as follows :

Fuse about 0.1 gm. of the ore in a covered platinum crucible with about 2 gms. of potassium bisulphate for about 10 minutes over a burner, at a dull red heat. Remove from the burner. Allow the melt to solidify on the wall of the crucible by holding it with a pair of nickel tongs in an inclined position. After the mass has solidified and the crucible has become cold to the touch, detach the mass by applying light pressure to the crucible. Dissolve it in 20 ml. of warm dil.  $\text{H}_2\text{SO}_4$  (1 : 4) in a 100 ml. beaker. Cool. Add 1-2 ml. of orthophosphoric acid and 2-3 ml. of hydrogen peroxide and shake. A yellow colour shows the presence of titanium in the ore. The addition of phosphoric acid is to depress the colour of ferric sulphate solution which is also yellow.

Dissolve 2 gm. ore sample in  $\text{HCl}$ . Bake, redissolve in  $\text{HCl}$ . Filter off the insoluble matter. From the filtrate, determine Al as  $\text{AlPO}_4$  by the method of Expt. 67. Iron is kept in the ferrous condition by means of sodium thiosulphate and the aluminium is thrown down either as the hydroxide or as aluminium phosphate. It is then ignited and weighed,

*Case II.* The ore contains titanium.

Dissolve 1 gm. ore in HCl. Filter off the insoluble matter. Ignite it and treat with HF and  $\text{H}_2\text{SO}_4$ . Fuse the residue left with  $\text{Na}_2\text{CO}_3$ . Dissolve in HCl. Add to the main filtrate. The resulting solution contains Al, Fe and Ti as chlorides. To determine Al and Ti separately from it two methods are available. One is due to Prof. Gooch. The principle underlying it is as follows :—

When  $\text{H}_2\text{S}$  is passed into an ammoniacal solution containing the chlorides of Al, Fe and Ti to which ammonium tartrate has been previously added, the iron alone is precipitated as FeS. This is filtered off, the filtrate acidified with  $\text{H}_2\text{SO}_4$ , the excess of  $\text{H}_2\text{S}$  expelled by boiling, the tartaric acid present destroyed by boiling with  $\text{KMnO}_4$  and the excess of the latter removed by  $\text{SO}_2$ . The titanium is then separated from Al by boiling with acetic acid. The former is thrown down as  $\text{TiO}_2$ , whereas the latter remains in solution. This is because of the hydrolysis of titanium acetate.

**Procedure :—**

Add tartaric acid equal to three times the weight of  $\text{Al}_2\text{O}_3 + \text{TiO}_2$  present in solution. Make neutral with  $\text{NH}_4\text{OH}$  s.g. 0.90 and then add 5 ml. of 1:1  $\text{H}_2\text{SO}_4$ . Pass  $\text{H}_2\text{S}$  until colourless. At this stage Fe is present in the bivalent condition. Now add  $\text{NH}_4\text{OH}$  in excess and pass  $\text{H}_2\text{S}$  until Fe is completely precipitated. Filter off FeS, wash with  $(\text{NH}_4)_2\text{S}$  (Bench-Reagent diluted twenty times with water). Acidify filtrate strongly with  $\text{H}_2\text{SO}_4$  and expel  $\text{H}_2\text{S}$  by boiling. Add a solution of  $\text{KMnO}_4$ , the volume of solution used containing  $\text{KMnO}_4$  equal in weight to  $2\frac{1}{2}$  times the weight of tartaric acid previously introduced. Boil. Clear with  $\text{SO}_2$  water. Cool. Add  $\text{NH}_4\text{OH}$  in slight excess and

then glacial acetic acid in considerable excess, 7 ml per 100 ml. of solution. Boil for 5 minutes when  $\text{TiO}_2$  is completely precipitated. Filter, wash with 7% acetic acid containing a few ml. of dil.  $\text{H}_2\text{SO}_4$ . (1:1) Reserve filtrate 'A' for Al determination. The residue is contaminated with a small amount of Al. To purify it proceed as follows :—

Ignite it in a platinum crucible. Fuse with 1 gm. anhydrous  $\text{Na}_2\text{CO}_3$ . Cool. Add 2.5 ml. of conc.  $\text{H}_2\text{SO}_4$ . Allow reaction to proceed in the cold. Warm. Pour the solution into 100 ml. water in a 600 ml. beaker. Add  $\text{NH}_4\text{OH}$  s.g. 0.96 until a precipitate just appears. Dissolve this in dil.  $\text{H}_2\text{SO}_4$  s.g. 1.2. Add 40-45 ml. glacial acetic acid, 20 gms. sodium acetate and 300 ml. water. Bring to a boil by rapid heating up and maintain at boiling heat for 1 minute. Filter. Wash with 7% acetic acid and then with water. Ignite in a platinum crucible, cool and weigh the titanium di-oxide.

Add the filtrate from the above to filtrate A. Precipitate Al from the combined filtrates by treatment with  $\text{NH}_4\text{OH}$ .

#### Alternative Method :—

This method for the separation of titanium from aluminium is due to Baudisch. Its principle is as follows:—

When cupferron ( See Expt. 37A, pp. 200,201 ) is added to a strongly acid solution containing Al and Ti, the latter is quantitatively precipitated. The reagent is the ammonium salt of nitroso phenyl hydroxylamine.

#### Procedure :—

Solution of cupferron : Dissolve 0.6 gm. in 10 ml. water. Dilute the solution of the chlorides of Al and Ti containing 30 ml. 6 N-HCl to 300-400 ml. with water. Add the reagent slowly. Allow the yellow precipitate

to settle. Ascertain by adding more of the precipitant whether precipitation is complete. If a white precipitate instead of a yellow one forms, the reagent is in excess. Filter through pulp, wash well with  $N\text{-HCl}$ , ignite the precipitate in a platinum crucible, at first slowly, to destroy organic matter and then strongly. The residue is  $\text{TiO}_2$ .

NOTES :—

(1) It is best to make the precipitation at  $0^\circ\text{C}$ .

(2) If the solution from which titanium is to be determined contains iron in addition to aluminium, the iron must be separated as  $\text{FeS}$  according to the method of Gooch described above. The filtrate from  $\text{FeS}$  is acidified with  $\text{H}_2\text{SO}_4$ , freed from  $\text{H}_2\text{S}$  by boiling, cooled and then treated with cupferron reagent.

(3)  $\text{Al}$  is determined from the filtrate from the titanium precipitate by evaporating to dryness with  $\text{H}_2\text{SO}_4$ , oxidising the residue of carbon with fuming nitric acid and then proceeding in the usual manner by adding  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$ .

(4) For every 100 ml. of the solution from which titanium is to be precipitated, there should be present 10 ml. of 1 : 1  $\text{H}_2\text{SO}_4$ ; otherwise,  $\text{Al}$  will contaminate the precipitate. The addition of 1-2 gms. of tartaric acid makes the separation very sharp.

(5) The reagent deteriorates in strong sun-light. It is best preserved in a cool, dark place. The introduction of ammonium carbonate wrapped in filter paper bags into a bottle of the reagent is also helpful in checking its deterioration.

**Procedure for  $\text{MnO}$ ,  $\text{CaO}$  and  $\text{MgO}$  :—**

Dissolve 2 gms. of the ore in  $\text{HCl}$ . Evaporate to dryness. Redissolve in  $\text{HCl}$ . Dilute with water.

**Filter.** Preserve filtrate (A). Ignite residue. Treat with HF and  $H_2SO_4$ . Dissolve the resulting residue in HCl. Add the solution to (A). Separate Fe, Al, Ti,  $P_2O_5$  by the basic acetate method of Expt. 21. From the filtrate, determine  $MnO$  as described thereunder. From the filtrate obtained by filtering off  $MnO_2$ , determine CaO and MgO as in Expt. 11.

### **Alkalies :—**

Dissolve 3 grams of the ore in HCl and a drop of  $HNO_3$ . Evaporate to dryness and redissolve in dil. HCl (1 : 1). Filter. Ignite residue, treat with HF and  $H_2SO_4$ , evaporate, boil residue with water acidulated with HCl, and add to the main filtrate. Neutralise. Add a slight excess of  $BaCl_2$  and filter. Heat filtrate to boiling. Add  $(NH_4)_2CO_3$ . Make up to 305 ml., let settle and take 200 ml. Evaporate to dryness. Heat gently. Extract residue with hot water, filter. Acidify filtrate with HCl, evaporate to dryness, ignite at low red heat. Cool and weigh as  $NaCl+KCl$ . Calculate %  $Na_2O+K_2O$  on the basis of 2gms. of the ore, after determining total Cl by titration with 0.02 N Ag.  $NO_3$

### **NOTE :—**

For a full account of the principles underlying the determination of alkalies, see Expt. 77. The modified procedure, in the case of the iron ore, described above is due to its ready solubility in HCl.  $BaCl_2$  transforms alkali sulphates into alkali chlorides.  $(NH_4)_2CO_3$  precipitates Fe as hydroxide and Ca, Mg and Ba as carbonates. Allowance is made for the volume of the precipitate by making up to 305 ml. instead of 300 ml. .

**Loss on Ignition :—**Ignite 0.5 gm. ore in a platinum crucible covered with lid. Cool and weigh.

### **Rapid Method for Mn :—**

Fuse 0.1 gm. ore with 2-3gms. of sodium bisulphate



in a platinum crucible for 15 minutes at a low red heat. Cool. Extract the melt with 10 ml. dil.  $\text{HNO}_3$  of s.g. 1.2. Add 10 ml. more of the same acid. Dilute to 30-40 ml. with water. Heat in a water bath. Add  $\text{AgNO}_3$  and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and proceed as in Experiment 22.

### **Rapid Method for $\text{TiO}_2$ :—**

The principle of the method is based on the fact that  $\text{H}_2\text{O}_2$  produces a yellow colour with  $\text{Ti}(\text{SO}_4)_2$  in dil.  $\text{H}_2\text{SO}_4$  (1:3). This colour is due to the formation of pertitanic acid. The depth of colour is proportional to the amount of titanium present.

**Standard Solution:**—Same as in Expt. 37, pp. 196, 197

### **Procedure for Ore :—**

Fuse 0.1-0.2 gm. of ore in a platinum crucible with 3 gms.  $\text{NaHSO}_4$ . Cool. Extract with dil.  $\text{H}_2\text{SO}_4$  (s.g. 1.2). Transfer to a graduated tube. Add 1 ml. pure  $\text{H}_3\text{PO}_4$  and 3-5 ml. of  $\text{H}_2\text{O}_2$  or  $\text{Na}_2\text{O}_2$  (0.5-1 gm.), in small quantities. Mix well. Pipette 1 ml. of the standard solution into a second graduated tube. Add  $\text{H}_2\text{O}_2$ . Make up to 100 ml. Mix well. Dilute the sample until its colour matches that of the standard.

### **Record of Results:—**

0.1 gm. ore taken.

1 ml. standard solution diluted to 100 ml.

This colour matched by the melt of ore on diluting to 20 ml.

$$\begin{aligned}\text{TiO}_2 \text{ in the ore} &= \frac{.001}{100} \times 20 \times 1000 \\ &= 0.2\%\end{aligned}$$

### **NOTE :—**

The addition of orthophosphoric acid depresses the colour due to ferric sulphate formed by the fusion of the ore.

**Phosphorus:**—See Expts. 14 and 16 for ‘Principle’ and for Solutions Required’.

Case I. Titanium is absent.

**Procedure :**— Dissolve a 2 gm. sample of the ore in 40 ml. conc. HCl. Evaporate to syrupy consistency. Add 25 ml.  $\text{HNO}_3$  ( s. g. 1.2 ). Without adding water, filter off the insoluble matter and wash filter and contents a few times with hot water. Heat the filtrate to boiling, add a solution of  $\text{KMnO}_4$  until a pink colour persists. Continue boiling for 3 minutes. Destroy excess  $\text{KMnO}_4$  with  $\text{Na}_2\text{SO}_3$ . Boil 2 minutes longer; cool to  $70^\circ\text{C}$ . Add 40 ml.  $(\text{NH}_4)_2\text{MoO}_4$ . Shake vigorously for 3 minutes. Filter and proceed with the alkalimetric titration as in the determination of phosphorus in steel.

Case II. Titanium is present.

**Procedure :**—

Dissolve 2 gms. ore in 40 ml. conc. HCl in a 200 ml. beaker. Evaporate to dryness. Redissolve in 20 ml. conc. HCl. Dilute with 30 ml. water. Filter and wash the residue with water. Reserve the filtrate (A). Ignite the residue in a platinum crucible. Fuse it with about 5 times its weight of  $\text{Na}_2\text{CO}_3$ . Extract the fusion with hot water. Filter off the residue in the residue the extract. Add the filtrate to A. Add 30 ml. conc.  $\text{HNO}_3$ . Evaporate to low bulk. Again add 30 ml. dil.  $\text{HNO}_3$  of s.g. 1.2 and proceed and finish as above.

**Record and calculation of results :**

$$\begin{array}{rcl}
 \text{Weight of Ore} & & = 2 \text{ gms.} \\
 \text{Volume of NaOH soln. (1 ml.} & = & .0002 \text{ gm. P)} = 20.0 \text{ ml.} \\
 \text{Volume of HNO}_3 \text{ (1 ml. HNO}_3 & = & 1 \text{ ml. NaOH)} = 14.0 \text{ ml.} \\
 \text{P} = & \frac{6 \times .0002 \times 100}{14} & = .06
 \end{array}$$

NOTES

When titanium is present in an ore, some of the phos-

phorus in the ore remains in the residue insoluble in hydrochloric acid. To recover this, fusion with  $\text{Na}_2\text{CO}_3$  is necessary. The fusion products are sodium titanate, ferric oxide, sodium phosphate and excess of  $\text{Na}_2\text{CO}_3$ .  $\text{Fe}_2\text{O}_3$  and sodium titanate are insoluble in hot water while the sodium phosphate readily dissolves in it. The filtrate containing the phosphate is added to the original filtrate from the insoluble residue, the determination then finished as usual. It should be noted that titanium dioxide forms two salts with  $\text{Na}_2\text{CO}_3$ . One has the formula  $\text{Na}_4\text{TiO}_4$  and the other  $\text{Na}_2\text{TiO}_3$ .

The latter, known as the meta titanate, is obtained from the first by treatment with hot water and is insoluble in it.

**Sulphur** :—See Expt. 18.

#### EXPERIMENT 57

### Complete Analysis of Vanadium-bearing Titaniferous Magnetite Ore.

The ore presents a variety of interesting analytical problems containing as it does titanium, iron, vanadium, manganese, etc. Titanium and iron cause interference not only in the determination of vanadium but they also cause interference in the determination of each other and vanadium causes interference in the determination of phosphorus.

The finely powdered ore is fused with potassium bisulphate thereby converting the iron into ferric sulphate, the titanium into titanium sulphate and the vanadium into vanadic acid. The silicious matter in the ore remains, after the fusion, as silica. The cold melt is extracted with dilute sulphuric acid. Tartaric acid is introduced into the solution and a current of hydrogen sulphide is then passed. The tartaric acid prevents vanadium from being thrown down as vana-

dium sulphide. Ammonium hydroxide is next added until the solution is ammoniacal and the current of hydrogen sulphide is continued. This throws down iron as ferrous sulphide. It is filtered off, ignited to oxide, the oxide dissolved in hydrochloric acid, the solution reduced by stannous chloride and the determination is completed by the usual procedure of adding mercuric chloride solution, followed by the addition of either standard potassium permanganate or potassium dichromate solution.

The filtrate from the residue of iron sulphide is evaporated to dryness in a platinum dish and then ignited to destroy tartaric acid and other organic matter. The residues from ignition are fused with a mixture of sodium carbonate and potassium nitrate and the fused mass extracted with boiling hot water and the solution filtered. The residue on the paper contains all the titanium as sodium metatitanate and the vanadium is in the filtrate as sodium vanadate, free from the elements that will interfere with its determination.

### **Determination of Titanium.**

#### **Principle :—**

When hydrogen peroxide is added to a solution of titanium sulphate a yellow colour is produced. The intensity of the colour produced is matched with the colour produced by a standard solution of titanium sulphate, similarly treated with hydrogen peroxide. This method is applicable to cases where the percentage of titanium does not exceed five. Where, as in the case on hand, the percentage exceeds this figure, the method that is adopted is known as the Jones Reductor Method. The principle of this is that when a solution of titanium sulphate is passed through a column of amalgamated zinc, the titanium is reduced from the quadrivalent to the trivalent condition. The titanous sulphate formed readily under-

goes atmospheric oxidation. Therefore it is collected in a solution of ferric sulphate. This oxidises the titanous sulphate and, in the process, forms an equivalent amount of ferrous sulphate. This latter is determined by the usual titration with standard permanganate solution.

### **Determination of Vanadium.**

#### **Principle :—**

When an acidified solution of potassium or sodium vanadate is treated with sulphurous acid, the vanadium is reduced from the penta to the quadrivalent stage. The excess of sulphurous acid is then expelled by boiling and the vanadium in the vanadyl sulphate solution is determined by titration with standard potassium permanganate solution, when the vanadium passes into the pentavalent condition.

### **Determination of Phosphorus.**

#### **Principle :—**

When ammonium molybdate is added to a solution containing phosphoric and vanadic acids, both are thrown down as precipitates. But if the vanadic acid is reduced to vanadyl sulphate either by ferrous sulphate or sulphurous acid and the precipitation is then made with ammonium molybdate, ammonium phospho molybdate, uncontaminated by ammonium vanado molybdate, is thrown down as a precipitate. This is filtered off, washed free of acid and precipitant and then dissolved in a standard solution of sodium hydroxide, using phenolphthalein as indicator. 1 ml. 0.2 N -NaOH = 0.00027 gm. P.

The procedure adopted was as follows :—

### **Determination of Iron.**

0.5 gm sample was fused with 5 gms. of potassium bisulphate in a platinum crucible of about 30 ml. capacity, covered with a lid, over a Bunsen burner at

dull red heat for 30 minutes. The cold melt was extracted with dilute sulphuric acid ( 1:9 ) and the solution was made up to 500 ml. exactly in a 500 ml. graduated flask using the same dilute acid. 100 ml. of the solution were pipetted off into a 400 ml. tall form beaker, 3 gms. of tartaric acid added, and a current of hydrogen sulphide passed for 15 minutes. Ammonium hydroxide s. g. 0.96 was next added until the solution was ammoniacal and then the current of hydrogen sulphide was continued for a further period of 15 minutes. The black precipitate of iron sulphide was filtered off, and a current of hydrogen sulphide was passed into the filtrate to ensure that no more iron was being precipitated. The precipitate was washed with hydrogen sulphide water to free it from titanium, vanadium, etc. It was then ignited with the filter paper in a porcelain crucible. The oxide obtained was brushed off into a 200 ml. beaker, 5 ml. concentrated hydrochloric acid were added to dissolve it and the same was heated gently for a few minutes. The solution was diluted with water to about 30 ml. and then boiled. The boiling hot solution was reduced with a solution of stannous chloride, added drop by drop from a dropping bottle until the solution became colourless and a few more drops of the reagent were then provided in excess. The cold and reduced solution of ferrous chloride was diluted with cold, distilled water to a volume of about 250 ml. The following reagents were then added in the order mentioned and, after the addition of each reagent, the solution was well stirred :—

(1) 10 ml. of a saturated mercuric chloride solution.

(2) 40 ml. of Zimmermann-Reinhardt reagent.

See Expt. 9, p. 59.

0.1 normal solution of potassium permanganate was then added from a burette until a pink colour persisting

for about a minute was obtained. 1 ml. of 0.1 normal  $\text{KMnO}_4 = 0.0056 \text{ gm Fe}$ .

### Procedure for Titanium

The filtrate from iron sulphide was cautiously evaporated to dryness in a platinum dish over a mushroom top burner, ignited to destroy organic matter and the residue fused with 2-3 gms. of sodium carbonate and 0.2 gm. of potassium nitrate. The fused mass when cold was boiled with water and filtered. The filtrate (F) was collected in a 500 ml. flask. The residue (R) on the filter paper containing the titanium as sodium metatitanate was fused with 2-3 gms. of potassium bisulphate converting the titanium into titanium sulphate. This was extracted with 30 ml. of dilute sulphuric acid (1 : 9). The solution was passed through the Jones Reductor, the solution caught in a 500 ml. flask containing 40 ml. of ferric sulphate solution, obtained by dissolving 4 gms. of the salt in 40 ml. of dil. sulphuric acid of 1.1 s.g. The Reductor tube was washed free of titanium salt by passing 100 ml. of dilute sulphuric acid of s.g. 1.05. The solution in the flask which is a mixture of ferrous sulphate, ferric sulphate and titanous sulphate was titrated against a decinormal solution of potassium permanganate until a pink colour lasting for a minute was obtained. 1 ml. 0.1 N— $\text{KMnO}_4 = 0.008 \text{ gm. TiO}_2$ .

### Procedure for Vanadium

The filtrate (F) was acidified with dilute sulphuric acid of s.g. 1.2. It was heated to boiling and then treated with a 2% solution of potassium permanganate until a distinct pink colour was seen. 5-10 ml. of normal sulphurous acid were then added to destroy the precipitate of manganese dioxide and to reduce the vanadium from the pentavalent to the quadrivalent condition. The excess of sulphur dioxide was expelled

by passing through the solution a current of carbon dioxide from a Kipp's generator. The vapours evolved were passed through 5 ml. of 1.01 s.g. sulphuric acid containing 2-3 drops of 0.03 normal potassium permanganate solution, persistence of the pink colour indicating the absence of sulphur dioxide in the vapours. The current of carbon dioxide was stopped and 0.03 normal potassium permanganate was added from a burette to the still hot solution (temperature 70°C—80°C) until a pink colour persisting for about a minute was obtained. A blank was run, using the same quantity of solid reagents and the same volume of liquid reagents as was introduced in the actual determination. The volume of 0.03 *N* potassium permanganate introduced to obtain a colour of the same intensity as in the determination was deducted and then the percentage of vanadium calculated.

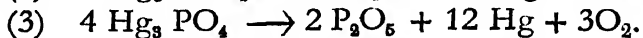
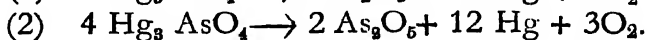
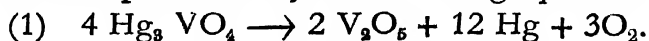
1 ml. of 0.0333 *N*— $\text{KMnO}_4$  = 0.0017 gm V.

As a check on the above procedure, vanadium was also determined by two alternative procedures. One of these is the classical method of Rose, as modified by Hillebrand.

(a) The principle of the first method is that when a sample of the ore is fused with a mixture of sodium carbonate and potassium nitrate, sodium vanadate, arsenate, phosphate, titanate and silicate are formed, the oxide of iron remaining unaffected. Extraction of the cold melt with boiling hot water and filtration yield a residue of sodium metatitanate and oxide of iron on the filter-paper. The filtrate contains all the other salts, as they are soluble in water. Addition of acid to neutralize all but the equivalent of 0.3-0.5 ml. *N*— $\text{HNO}_3$  of the alkaline carbonate and concentration to low bulk by evaporation followed by filtration yield silica and titania as a residue. On treatment of the filtrate with



a neutral solution of mercurous nitrate, mercurous arsenate, phosphate and vanadate are thrown down as a mixed precipitate. This is filtered off and ignited in a platinum crucible. The product of ignition is a mixture of all the vanadium which was present in the ore, and a small amount of phosphorus, both in the form of their pentoxides, and is weighed. This is then fused with sodium carbonate and the phosphoric acid in the cold melt determined by the method already outlined. After conversion into  $P_2O_5$ , a deduction is made from the combined weight of  $V_2O_5$  and  $P_2O_5$ . The difference gives  $V_2O_5$ , from which the percentage of vanadium is calculated. The changes taking place on ignition are represented by the following equations :—



$V_2O_5$  melts at  $690^\circ\text{C}$ . but does not decompose. The arsenic pentoxide decomposes into arsenic trioxide and oxygen. The former sublimes at about  $190^\circ\text{C}$ .  $P_2O_5$  is also volatile but some of it is retained by  $V_2O_5$ .

(b) The principle of the other method is based upon the solubility in hydrochloric acid of the mineral coulsonite which is the form in which the vanadium is present in the ore and which has been assigned the formula  $\text{FeO}, (\text{Fe}, \text{V})_2\text{O}_3$  and the insolubility of iron titanate ( ilmenite ) in this medium. The solution is filtered, and the filtrate treated with a mixture of sodium hydroxide and sodium peroxide. This treatment throws down iron as ferric hydroxide along with any small amount of titanium that may have dissolved. The precipitate is filtered off. The filtrate is acidified with dilute sulphuric acid, boiled with 2% potassium permanganate solution, the excess destroyed by sulphurous acid, the excess of the latter expelled by passing

CO<sub>2</sub> from a Kipp's generator and the determination completed as already described.

### **The Procedure Adopted**

(a) Method of Rose :—1 gm. sample of the ore was fused with 6 gms. of sodium carbonate and 0.5 gm. of potassium nitrate in a 30 ml. platinum crucible over a blast lamp. The cold melt was boiled with 200 ml. water in a 400 ml. beaker after the addition of a few drops of alcohol to decompose the green sodium manganate that was formed and the solution filtered. The filtrate was treated with dilute nitric acid of normal strength, added from a burette until the volume of the acid was short by about 0.2 to 0.5 ml. of the volume of the acid of the same strength required for a blank using the same weights of sodium carbonate and potassium nitrate, and heating the mixture for the same length of time as in the run. The solution was evaporated until nearly dry and the residue was boiled with 100 ml. water, and filtered. The filtrate was cooled to room temperature and then treated with a freshly prepared and neutral solution of mercurous nitrate in small additions until no more precipitate was formed. The precipitate was allowed to settle, filtered off, ignited in a platinum crucible, and weighed. The residue was fused with about half a gram of sodium carbonate and the cold melt dissolved in water. The solution was acidified with dilute nitric acid, the vanadic acid reduced with 3-5 ml. of 0.1 normal ferrous sulphate, the solution heated to 70°C and treated with 30 ml. of acid ammonium molybdate solution, well shaken, and the precipitate of ammonium phosphomolybdate filtered, washed free of acid with 1% potassium nitrate solution and the precipitate transferred to the

vessel in which the precipitation was made, well shaken with 20 ml. water and then titrated with 0.2 normal sodium hydroxide solution, using phenolphthalein as indicator. The weight of phosphorus calculated to  $P_2O_5$  was deducted from  $V_2O_5 + P_2O_5$ , already obtained. The difference gives  $V_2O_5$ .

(b) Procedure for Vanadium :—2gm. sample was digested at room temperature with 40 ml. conc. hydrochloric acid for a period of 2-3 hrs. in a 150 ml. flask. The contents of the flask were then transferred to a 400 ml. beaker and then evaporated to low bulk with the addition of 10 ml. concentrated nitric acid. This was then taken up in 20 ml. dil. hydrochloric acid, diluted with water to about 30 ml. and filtered. The filtrate (G) was collected in a 400 ml. beaker. The filter paper with the residue was washed free of iron, ignited in a platinum crucible and the ignited residue twice evaporated to dryness, each time using about 3 ml. conc. nitric acid and 5 ml. hydrofluoric acid, added in this order. The residue was again evaporated with nitric acid alone twice, each time using 5 ml. of the acid. The contents of the crucible were ignited strongly and fused with 2 gms. sodium carbonate and 0.2 gm. potassium nitrate, the cold melt extracted with hot water and treated with dilute hydrochloric acid until acid and the solution added to the main filtrate (G). The combined filtrate was neutralized with a 14% solution of caustic potash. Care was taken that no persistent precipitate was formed in the process. The solution was boiled, transferred to a tap funnel and the solution was then run in drops into 100 ml. of a freshly prepared and hot solution of potassium hydroxide of the same strength as above (14%) and containing 3-4 grams of sodium peroxide. This operation throws down the iron and titanium, if any, as hydroxides whereas aluminium, phosphorus and

vanadium remain in solution. The tap funnel was rinsed twice with water and the solution was boiled and filtered to free it from iron and titanium hydroxides. The filtrate (H) was received in a 700-800 ml. flask. The residue was redissolved in 20 to 30 ml. conc. hydrochloric acid and the processes of neutralization with KOH, adding, from a tap funnel, this neutralized solution to 100 ml. of a hot 14% KOH solution containing 1-2 gms. of sodium peroxide, boiling and filtering were repeated. The filtrate obtained was added to the main portion (H). The repetition of the process has for its object the recovery of any vanadium that may be occluded by the rather bulky precipitate of ferric hydroxide.

The combined filtrates were neutralized with dilute  $\text{H}_2\text{SO}_4$  (s.g. 1.2) and a little excess of it added. The solution was then treated with a 2%  $\text{KMnO}_4$  solution until it was coloured pink. The further procedure from this point was exactly the same as was described under 'Procedure for vanadium'.

### Procedure for Phosphorus

1 gm. sample of the ore was sintered in a nickel crucible with 3-4 gms. of sodium peroxide, the mass extracted by immersing the cold crucible in 200 ml. of hot water contained in a 400 ml. beaker. The solution was boiled and filtered. Dilute  $\text{HNO}_3$  of S.G. 1.2 was added to the filtrate until it was acid and then 3-4 ml. more. 3-5 ml. of 0.1 normal ferrous sulphate solution were next added. This was followed by the addition of 6 gms. of ferric nitrate crystals, a few drops of normal sulphurous acid. and then the solution was heated up to  $70^\circ\text{C}$ . 30 ml of acid ammonium molybdate were next added, the mixture was well shaken and the precipitate allowed to settle for 48 hours. This was filtered off, washed with 1%  $\text{KNO}_3$  solution to free

it from ferric salts, molybdate reagent and acid. The filter paper with the precipitate was then transferred to the vessel in which the precipitation was made, 20 ml. of water added, the contents well shaken, a few drops of phenolphthalein added and then 0.2 normal sodium hydroxide solution added from a burette until a pink colour was obtained.

### Determination of Manganese.

Manganese is oxidised from the bivalent to the heptavalent condition in nitric acid solution by sodium bismuthate. This reagent oxidises vanadium also from the quadri to the pentavalent condition. The permanganic and the vanadic acids are treated with a measured excess of a standard solution of ferrous sulphate and the excess of the latter then obtained by adding from a burette a standard solution of  $\text{KMnO}_4$ . If the two solutions are of equal strength, then the difference between the two volumes used is a measure of the amount of manganese. 1 ml. of  $0.03\text{NFeSO}_4 = 0.00033$  gm. Mn.

Procedure :—0.1 gm. sample of the ore was fused with 3-4 grams of potassium bisulphate in a platinum crucible and the fusion was extracted with 20 ml. dil  $\text{HNO}_3$  of s.g. 1.2. The cold solution was treated with 0.5 gm. of sodium bismuthate and well shaken for 3-4 minutes. This solution was then filtered through asbestos filter pad contained in a Gooch crucible, to free it from excess of bismuth tetroxide, which is a product of the decomposition of the bismuthate. To the filtrate a known excess (about 20.0 ml.) of 0.03 normal ferrous sulphate was added from a burette and then 0.03 normal  $\text{KMnO}_4$  was added until a pink colour was obtained. The solution was then heated up to about  $70^\circ\text{C}$ ., and the permanganate addition made until a pink colour persisting for about a minute was obtained.

The object of heating up to  $70^{\circ}\text{C}$  towards the end of the titration is to ensure that the vanadium which was in the pentavalent condition before the introduction of ferrous sulphate is restored to that very condition at the end of the titration. In cold solution, this is not quantitatively effected by  $\text{KMnO}_4$  solution but at the temperature specified ( $70^{\circ}\text{C}$ ) the oxidation becomes quantitative. . It must be remembered that ferrous sulphate reduces both permanganic and vanadic acids formed by the action of bismuthate. The permanganate addition restores the vanadium to its original condition but is without effect on the reduced manganese.

### Determination of Silica.

1 gm. sample of the ore was fused with 4-5 gms. of potassium bisulphate in a covered platinum crucible at dull red heat for about one hour. The cold melt was extracted with dilute sulphuric acid (1:9) and filtered. The residue with the paper was ignited and the fusion, extraction and filtration repeated. The final residue with the filter paper after freeing from iron and potassium salts was ignited in a platinum crucible and weighed. The crucible and contents were treated with 1 ml. dil  $\text{H}_2\text{SO}_4$  (s.g. 1.2) and 10 ml. HF and evaporated to fumes. The treatment with the acids and the evaporation were repeated and the residue heated strongly at  $800\text{--}900^{\circ}\text{C}$ , the crucible cooled in a desiccator and weighed. The difference between the original weight and the final weight represents the silica.

The results of analysis of the sample are :—

Fe calculated to $\text{Fe}_3\text{O}_4$	72.03%
$\text{V}_2\text{O}_5$	1.57%
$\text{TiO}_2$	17.80%
$\text{MnO}$	0.20%
$\text{P}_2\text{O}_5$	0.11%
$\text{SiO}_2$	1.23%

## EXPERIMENT 58.

**Complete Analysis of Manganese Ore.**

The following are determined :—

$\text{SiO}_2$ ,  $\text{MnO}$ ,  $\text{MnO}_2$ ,  $\text{Fe}$ ,  $\text{S}$ ,  $\text{P}$ ,  $\text{BaO}$  and  $\text{CaO}$ .

**Silica :—**

Dissolve 1 gm. of the ore in 15 ml. conc.  $\text{HCl}$  in a 150 ml. casserole with cover-glass on. Evaporate to dryness. Redissolve in  $\text{HCl}$ . Take to low bulk. Add 8-10 ml. (1:1)  $\text{H}_2\text{SO}_4$  and evaporate to fumes. Cool. Boil with 100 ml. water. Filter. Wash. Transfer filtrate (A) to a 500 ml. measuring flask. Make up to the mark. Ignite residue in a platinum crucible. Weigh. The weight represents the weight of the crucible and the residue of silica and barium sulphate. Treat with  $\text{HF}$  and  $\text{H}_2\text{SO}_4$ . Ignite and weigh. The loss represents  $\text{SiO}_2$ .

**Procedure for  $\text{BaO}$  :—**

Fuse the residue left after this treatment with about 1 gm.  $\text{Na}_2\text{CO}_3$ . Extract with water. Filter. Dissolve the residue in dil.  $\text{HCl}$  of s.g. 1.1. Neutralise excess acid with  $\text{NH}_4\text{OH}$ . Add 1-2 ml.  $\text{HCl}$ . Precipitate as  $\text{BaSO}_4$  by the addition of dil.  $\text{H}_2\text{SO}_4$ . Filter, ignite and weigh as  $\text{BaSO}_4$ . Calculate to  $\text{BaO}$ .

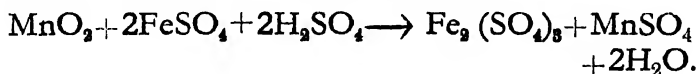
**Procedure for  $\text{Mn}$  :--**

Pipette off 100 ml. of filtrate (A) into a 400 ml. beaker. Heat to boiling. Add zinc oxide emulsion until the free acid is neutralised,  $\text{Fe}(\text{OH})_3$  is thrown down as a ppt. and a slight excess of zinc oxide is present which is indicated by the milky appearance of the upper layer of liquid. Filter. Proceed by the Volhard method the principle of which is as follows :—

When a neutral and boiling hot solution of manganous sulphate is treated with a standard solution of  $\text{KMnO}_4$ ,  $\text{MnO}_2$  is thrown down as a ppt. Comple-

tion of the precipitation is indicated by the appearance of a pink colour. This gives the total Mn, that is, Mn present as MnO and that present as MnO<sub>2</sub>. To determine MnO<sub>2</sub> proceed as follows :—

Introduce 1 gm. ore into a 500 ml. flask. Also introduce 10 gms. ( exactly weighed ) of FeSO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 6H<sub>2</sub>O into it. Add 100 ml. dil. H<sub>2</sub>SO<sub>4</sub> s. g. 1.3 and a calcite crystal. Close the mouth with a one holed cork. Boil until no dark particles of ore are seen. Introduce calcite crystals into the flask and cool. Add 0.1-N KMnO<sub>4</sub> until a pink colour persists. The volume of KMnO<sub>4</sub> used gives the excess of FeSO<sub>4</sub>. By difference the amount of FeSO<sub>4</sub> used up is obtained. From this the manganese present as MnO<sub>2</sub> is calculated. From the total Mn and that present as MnO<sub>2</sub> the quantity present as MnO is obtained. The reaction is :—



Notes on the Volhard Method :—

(1) Manganese ore is always associated with a certain amount of iron. This goes into solution along with Mn. Volhard's method is applicable only when the iron is removed as Fe (OH)<sub>3</sub> by precipitating with zinc oxide. Other precipitants like NH<sub>4</sub>OH or NaOH will precipitate both Fe and Mn as hydroxides.

(2) Much of the free sulphuric acid may be neutralised by a solution of Na<sub>2</sub>CO<sub>3</sub> before the introduction of zinc oxide emulsion.

•(3) To prevent the precipitation of Mn by any inadvertent, liberal addition of zinc oxide, 2 gms. of ZnSO<sub>4</sub> are added prior to the addition of ZnO.

(4) The zinc oxide used must be free from ZnCO<sub>3</sub>. As ordinarily obtained, it contains some ZnCO<sub>3</sub>. It is best, therefore, to ignite immediately before use the



oxide in a nickel or platinum crucible to decompose any carbonate of zinc. The presence of carbonate will tend to remove a part of Mn as  $\text{MnCO}_3$  along with  $\text{Fe}(\text{OH})_3$ , thus causing low results for Mn.

(5) The addition of a few drops of dil.  $\text{HNO}_3$  (s.g. 1.2) just before titration facilitates the gathering together and settling down of  $\text{MnO}_2$  precipitate and hence the end point is sharply indicated.

(6) In the case of unknown ores, it is best to heat to boiling for a minute or two the assay solution, the titration of which is apparently finished, to see if the pink colour persists; if it does not persist, a few more drops of  $\text{KMnO}_4$  are added until the pink colour persists. The final reading is then taken. To catch the end-point, support the flask as in Fig. 20.

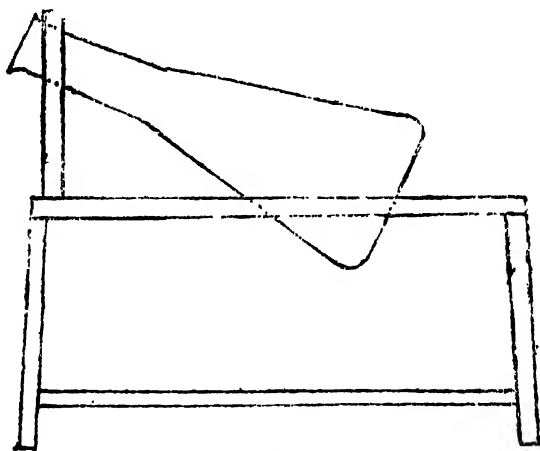


Fig. 20.

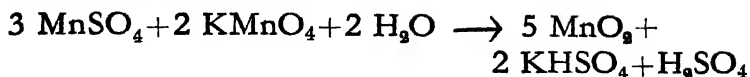
Record and Calculation of Results for total Mn —

Weight of ore taken 1.0000 gm.

Solution was made up to 500 ml. exactly.

100 ml. Soln. ( = 0.2 gm. sample ) consumed 70.0  
ml. of 5/56 N  $\text{KMnO}_4$

From the equations :—



$10 \text{ FeO} + 2 \text{ KMnO}_4 \longrightarrow 5 \text{ Fe}_2\text{O}_3 + \text{K}_2\text{O} + 2 \text{ MnO}$ , it follows that

2 gm.-moles of  $\text{KMnO}_4 = 10 \text{ gm.-atoms of Fe}$   
 $= 3 \text{ gm.-atoms of Mn}$

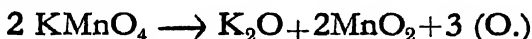
(i. e.)  $10 \times 56 \text{ gms of Fe} = 3 \times 55 \text{ gms. of Mn.}$

$$1 \text{ gm. Fe} = \frac{3 \times 55}{10 \times 56} \text{ gm. Mn.}$$

1 ml. of  $5/56 \text{ N KMnO}_4 = 0.005 \text{ gm. Fe gm.}$   
 $= 0.001473 \text{ gm. Mn.}$

Mn content of the ore  $= 500 \times 70 \times 0.001473 = 57.00\%$

An alternative method of calculation is based on the following principle:—In the presence of a reducing agent and in a neutral medium,  $\text{KMnO}_4$  decomposes as follows :—



The permanganate solution which is  $5/56 \text{ N}$  in acid medium will therefore be  $\frac{5}{56} \times \frac{6}{10}$  or  $\frac{3}{56} \text{ N}$  in neutral medium. 1 ml. of  $3/56 \text{ N KMnO}_4 = 0.001473 \text{ gm. Mn.}$

**Procedure for Fe :—**

Proceed exactly as in Experiment 10.

**Procedure for  $\text{Al}_2\text{O}_3$  :—**

Dissolve 1 gm. in 20 ml.  $\text{HCl}$  in a 150 ml. covered casserole. Evaporate to low bulk. Again add 10 ml.  $\text{HCl}$ . Evaporate to dryness. Take up with 20 ml. of dil.  $\text{HCl}$  (1:1). Filter. Reserve filtrate (A). Ignite residue in a platinum crucible. Cool. Weigh. Treat with  $\text{HF} + \text{H}_2\text{SO}_4$ . Evaporate to fumes. Extract the residue left with  $\text{HCl}$ . Add to (A). Precipitate Fe and Al as basic acetates as in Experiment 21. Filter. Dissolve the

residue in HCl and determine Al as  $\text{AlPO}_4$  as in Expt. 67. From the filtrate throw down Mn as  $\text{MnO}_2$  ( Expt. 21 ). Filter off  $\text{MnO}_2$ . From the filtrate determine CaO as in Expt. 11.

### Procedure for S :—

That portion of S in the ore which can be dissolved in aqua regia is determined as shown in Experiment 18.

That portion of S present as  $\text{BaSO}_4$  is determined by fusion of the residue insoluble in aqua regia with 'fusion mixture' in a platinum crucible. This yields  $\text{BaCO}_3$  and  $\text{Na}_2\text{SO}_4$ . The latter is soluble in water and therefore separated from the former by solution in water and filtration. Acidify filtrate with HCl. Evaporate to dryness. Take up with HCl. Filter off any residue of  $\text{SiO}_2$ . Adjust acidity and add  $\text{BaCl}_2$ . Filter, ignite and weigh the residue of  $\text{BaSO}_4$ . From the two experiments calculate the total sulphur.

### Phosphorus :—

Dissolve 2 gms. of the ore in  $\text{HCl}$ . Evaporate to dryness. Redissolve in HCl. Filter off insoluble matter. Ignite it in a platinum crucible, treat with HF and  $\text{H}_2\text{SO}_4$ . Add the resulting sulphate solution to the original filtrate. Add ammonia until a precipitate forms. Redissolve in  $\text{HNO}_3$ , heat to  $70^\circ\text{C}$ , add  $(\text{NH}_4)_2\text{MoO}_4$  and finish by the alkalimetric titration of Expt. 16.

**Organic Matter and loss on ignition:—**For the determination of these, proceed as in Experiment 56.

## EXPERIMENT 59.

### Complete Analysis of a Copper ore.

**Silica :—**Dissolve 1 gm. of the finely ground ore in 20 ml.  $\text{HNO}_3$  (s.g. 1.2) in a 150-200 ml. casserole. Cover with a cover glass, evaporate to dryness, take up in HCl, dilute, boil, filter, wash, ignite and weigh  $\text{SiO}_2$  and insoluble matter.

**Sulphur :—**

Boil filtrate, add 10 ml. of 10%  $\text{BaCl}_2$  solution, boiling hot, allow precipitate to settle on a hot plate at about  $100^\circ\text{C}$ . for 1 hour, filter, wash, ignite in a porcelain crucible at a dull red heat and weigh as  $\text{BaSO}_4$ .

**Copper :—**

Remove the excess of  $\text{BaCl}_2$  in the above filtrate by adding  $\text{H}_2\text{SO}_4$ , evaporating near to dryness, taking up with  $\text{H}_2\text{O}$ , filtering off the precipitate of  $\text{BaSO}_4$  and discarding the same. Determine the copper from the filtrate as in Experiment 43. Principle and procedure for determining copper only in an ore are described fully at the end of this expt.

 **$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$  :—**

Add 2 ml.  $\text{HNO}_3$  to solution left after separation of Cu by electrolysis, and precipitate Fe, Al and P by the 'basic acetate' method of Experiment 21. Filter, wash, ignite and weigh as  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$ . Call the filtrate (F). Dissolve the residue in HCl and determine Al as  $\text{AlPO}_4$  by the method shown in Expt. 67.

Acidify the filtrate from  $\text{AlPO}_4$  with dil. HCl, boil off  $\text{SO}_2$ , filter off sulphur, reduce filtrate with  $\text{SnCl}_2$  and determine Fe as shown in Experiment 10.

Determine P on a fresh sample. Proceed as follows :—

Dissove 2-5 gms. of the sample in 30 ml.  $\text{HNO}_3$  (s.g. 1.2), in a 200 ml. beaker, add HF in drops at a time, using about 2 ml. in all, evaporate to low bulk. Filter and precipitate P as  $(\text{NH}_4)_3\text{PO}_4$ ,  $12\text{MoO}_3$  from the filtrate by the method of Expt. 16 and finish as shown thereunder.

Make the filtrate (F) from the precipitation of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ , alkaline with  $\text{NH}_4\text{OH}$ , warm and pass  $\text{H}_2\text{S}$ , filter off any precipitate of Zn, Mn, Ni and Co. Wash. Reserve the filtrate  $F_1$  for the determination of Ca and Mg.

**Manganese<sup>1</sup> :—**

Dissolve the precipitate in hot conc. HCl with a little conc. HNO<sub>3</sub>, add 20 ml. NaC<sub>2</sub>H<sub>3</sub>O<sub>3</sub> ( 7 gms. salt in 20 ml. water ) and again pass H<sub>2</sub>S. Filter. The residue consists of Zn, Ni and Co sulphides. Mn is in the filtrate. Determine it by the method shown in Expt. 22 after evaporating the solution to low bul. with dil. HNO<sub>3</sub> of s.g. 1.2.

**Cobalt<sup>1</sup> :—**

Dissolve the precipitate containing Zn, Ni and Co in aqua regia, make alkaline with KOH, add acetic acid until the solution is acid and then add conc. solution of KNO<sub>2</sub> equal to half the volume of solution, allow to stand for 24 hours, filter, wash with 10% solution of C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>K, dry and ignite the potassium cobalt nitrite precipitate, moisten with a little ( 1 : 1 ) H<sub>2</sub>SO<sub>4</sub> and re-ignite. The precipitate has the composition 2CoSO<sub>4</sub> + 3K<sub>2</sub>SO<sub>4</sub>. Factor = 0.1417.

**Nickel<sup>1</sup> :—**

To the filtrate from Co precipitation, add NH<sub>4</sub>Cl and NH<sub>4</sub>OH, just acidify with HCl, boil and add 20 ml. of a 1% alcoholic solution of dimethyl glyoxime, make just ammoniacal and precipitate Ni, filter, transfer the moist precipitate to a porcelain crucible, dry at the mouth of a muffle furnace and gradually push into the hot part. Ignite at 800°C. Cool and weigh as NiO.

**Zinc<sup>1</sup> :—**

Decompose the excess of glyoxime in the filtrate by boiling it with 10 ml. conc. HCl. Make alkaline with ammonia ; pass H<sub>2</sub>S until freely smelling of H<sub>2</sub>S, filter, wash, ignite carefully and weigh as ZnO.

**Calcium Oxide :—**

Boil off H<sub>2</sub>S from the filtrate 'F,' obtained from the

precipitation of Zn, Mn, Ni and Co ; add  $\text{NH}_4\text{OH}$  and 10 ml. of 10%  $\text{NH}_4\text{Cl}$ , boil and add 20 ml. of 12%  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , allow to stand, filter, wash free of precipitant, dissolve the precipitate in 5 ml. dil.  $\text{H}_2\text{SO}_4$  of 1.2 s.g., heat to  $70^\circ\text{C}$ . and titrate against 0.05 N- $\text{KMnO}_4$  as in Expt. 11 Calculate to  $\text{CaO}$ .

#### **MgO :—**

To the filtrate add 50 ml. of  $\text{NH}_4\text{OH}$  of 0.90 s.g. and 5 ml. of a 20% solution of  $(\text{NH}_4)_2\text{HPO}_4$  with constant stirring, allow to settle, filter, wash with dil.  $\text{NH}_4\text{OH}$  (1 : 10), dry, ignite and weigh as  $\text{Mg}_2\text{P}_2\text{O}_7$ .

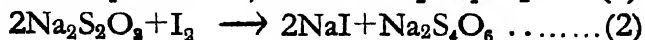
#### **Silver and Gold :—**

These are determined by a combination of wet and dry assay methods described in Experiment 53.

#### **Determination of Copper :—**

##### **Principle :—**

When potassium iodide is added to a solution of copper sulphate in water, iodine is liberated. By titrating the liberated iodine against a standard solution of sodium thiosulphate, using freshly prepared starch solution as indicator, the amount of copper can be determined. The reactions that take place are represented by the following equations :—



From equation (1) it is clear that 1 gram-atom of free iodine corresponds to 1 gram-atom of copper.

**Solutions Required :—**Shown at the end of this exercise.

##### **Procedure :—**

Weigh 1 gm. sample of the finely powdered ore in a 250 ml. casserole. Use a cover glass. Add 10 ml. conc.  $\text{HCl}$  and heat on the hot plate for 10-15

minutes. Add 10 ml. conc.  $\text{HNO}_3$  and heat until the ore is completely dissolved. If sulphur globules appear, add 0.5 gm.  $\text{KClO}_3$  and heat until they disappear. Evaporate to fumes with 10 ml. of 1:3  $\text{H}_2\text{SO}_4$ . Cool. Add 30 ml. of water cautiously. Boil until all soluble matter dissolves. Filter off the insoluble matter. Wash the filter paper and residue free of copper with 1:5  $\text{H}_2\text{SO}_4$ . Reject the residue. Add 4 gms. of granulated zinc to the filtrate. The solution becomes colourless in about 4-5 minutes after the addition of zinc. Heat to dissolve the excess of zinc. Add 25 ml. of a saturated solution of hydrogen sulphide in water to precipitate traces of copper which may still be left in solution.

Filter and wash with water saturated with hydrogen sulphide until the filtrate is free from soluble iron salts. Perform the test as follows:—Collect 5 to 10 ml. of the filtrate in a clean test-tube, boil to expel hydrogen sulphide, add 2 to 3 drops of conc.  $\text{HNO}_3$ , shake, cool, dilute to 20 ml. with water, add a few drops of a solution of ammonium or potassium sulphocyanide. Absence of a red color indicates that the filtrate is free from iron salts. Transfer the metallic residue on the filter-paper by means of the wash bottle jet to the casserole in which the copper was precipitated by zinc. Not much water is to be used in the act of transfer of residue. 10 ml. of it will do. Cover with a cover glass. Add through the spout 10 ml. conc.  $\text{HNO}_3$  to the casserole with the residue of copper. Heat until dissolved. Pour the hot solution on to the filter-paper. Any residue of copper adhering to the paper is dissolved by this means. To dissolve any sulphide of copper which may still remain on the paper, pour on to it 5 ml. of bromine-water, receiving the filtrate in the same casserole in which the main bulk of the solution of copper residue in  $\text{HNO}_3$  is contained.

Wash the filter-paper 5 or 6 times with hot water collecting the washings in the same casserole.

By proceeding as described above a solution of Cu in  $\text{HNO}_3$  free from iron, which was associated with the ore, is obtained. The volume of the solution at this stage should not exceed 75 ml.

Boil this solution vigorously for about 10 minutes until the bromine is completely expelled. Expulsion may be considered complete when volume is reduced to about 40-50 ml. Cool. Add ammonia (s. g. 0.90) until the solution becomes just blue. Boil 2-3 minutes. Add acetic acid (Bench Reagent) until the smell of ammonia is destroyed, then add 2-3 ml. of glacial (i. e.,) conc. acetic acid. Cool to room temperature. Dilute to about 50 ml. with distilled water.

Add 3 gms. of KI. Due to the liberated iodine and the solution of the same in the excess of KI, the liquid becomes brown. Run from a burette standard sodium thiosulphate solution. The brown colour changes gradually deep yellow. When the yellow colour has become faint, introduce 5 ml. of freshly prepared starch solution. A deep-blue colour is developed. Continue to run the thiosulphate solution until the blue colour becomes faint, or, is just destroyed. The blue colour must not reappear until after the lapse of about 5 minutes. If it reappears earlier, the experimental details given above have not been strictly adhered to. In this case the determination will have to be repeated.

#### **Calculation :—**

If 1 ml. of thiosulphate solution equals 0.005 gm. Cu and if in an assay on 1 gm. sample 40.0 ml. of the thiosulphate solution have been used up to reach the end-point, then the percentage of copper is 20.



## NOTES :-

(1) The method of 'Opening out' depends on the nature of the ore. Oxidised and partially oxidised ores are opened out as described. Copper concentrate, on the other hand, is more readily and easily opened out by concentrated nitric acid containing potassium chlorate dissolved in it at room temperature. The desirable proportions are 100 ml. conc. nitric acid to 10 gms. potassium chlorate. Use at the rate of 20 ml. of this mixture per gm. of concentrate. The process of solution and the fuming with conc. sulphuric acid are very conveniently and expeditiously carried out in a 100 ml. Jena or Pyrex flat-bottomed flask which can be manipulated over a bare flame by using a wire flask-holder. An alternative procedure for opening out the concentrate consists in dissolving it in a mixture of conc. nitric acid and liquid bromine. 20 ml. of conc. nitric acid and 1 ml. of liquid bromine are suitable quantities for 1 gm. concentrate. This mixture should be allowed to act on the concentrate for 5-10 minutes at room temperature in the wash-bottle shaped Jena flask, when the solution should be completed by boiling. In either case fuming with sulphuric acid should follow solution.

(2) In washing the residue of copper and copper sulphide free of iron, great care must be taken not to allow the filter paper to drain completely. The addition of wash-liquid, namely  $H_2S$  water, must be made while there is still some liquid left on the filter-paper. If this is not done,  $CuS$  will be oxidised by atmospheric oxygen to basic sulphate and will then pass into the filtrate.

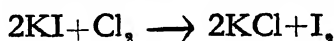
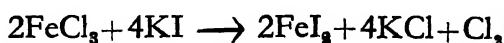
(3) The iodide method of determining copper can be carried out only when no free mineral acids are present in solution.

(4) The reagents used must be the purest obtainable.

The potassium iodide used must be free from potassium iodate. Test as follows:—

Dissolve 0.5 gm. of KI in 5 ml. of water, add 1-2 ml. of dil.  $\text{H}_2\text{SO}_4$  (1:5) and a few drops of freshly made starch solution. No blue colour must develop within 5 minutes.

(5) The copper ore is always associated with iron-oxide or pyrites, and sometimes with arsenic and antimony. Before the addition of KI, it is necessary to remove the iron. If this is not removed, the percentage of copper returned will be high. The following reactions will make the point clear:—

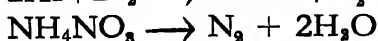
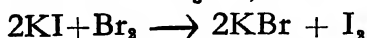
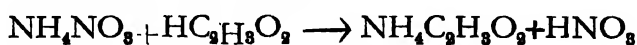


Arsenic and antimony are reduced when present in an ore to arsenious and antimonious acids during the deposition of copper. These acids form arsenide and antimonide of Cu to a certain extent. By dissolving the deposited copper in a mixture of  $\text{HNO}_3$  and bromine-water, arsenic and antimony are oxidised to the pentavalent condition. In this condition, they do not interfere with the assay but when present in the trivalent condition, a lower value is obtained for the assay. This will be evident from the following reactions:—



The addition of starch solution must be made towards the end when the colour is light yellow. If added at the beginning, the blue coloured compound of iodine and starch is formed in large amount and is not easily decomposed by the thiosulphate solution. The percentage of Cu obtained will therefore be slightly lower.

(6) The solution to which KI is to be added must not contain any nitrous acid, nitric acid, or bromine-water. When copper dissolves in  $\text{HNO}_3$ , a certain amount of  $\text{HNO}_2$  is formed. This is neutralised by ammonia forming ammonium nitrite. When the solution is boiled, the ammonium nitrite decomposes into nitrogen and water. Both  $\text{HNO}_2$  and  $\text{Br}_2$  when present will register a higher value for copper. The following reactions will make this clear:—



(7) The solution to which KI is to be added must contain free acetic acid. Too much ammonia added to neutralise the free mineral acids is harmful in that ammonium acetate is formed on the subsequent addition of  $\text{CH}_3\text{COOH}$  in large amounts which salt prevents the reaction between KI and  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$  from proceeding to completion.

(8) Aluminium is also used in place of zinc for depositing copper; but its action is slow.

(9) As an alternative to precipitation of copper by means of zinc or aluminium, the precipitation as copper sulphide can be made, the sulphide ignited in a porcelain crucible to oxide, the oxide dissolved in dil.  $\text{HNO}_3$  (1 : 3) in the crucible itself, the solution transferred to a 200 ml. conical flask, and the determination finally carried out by the iodide method as already described.

#### **Procedure for precipitation as CuS and finishing :—**

Boil the mass resulting from the fuming operation with 20-30 ml. water and filter. Collect the filtrate in a 600 ml. beaker. Wash the flask and filter-paper

5-6 times with warm water. Dilute the filtrate to a volume of 300 ml. Heat to boiling. Pass a rapid stream of hydrogen sulphide until the contents of the beaker fall to room temperature. This will take 20-30 minutes. Filter off the sulphide of copper. Collect the filtrate in a second beaker, heat it to boiling and repeat passing hydrogen sulphide to ensure that no more copper is present. In washing the precipitate of copper sulphide, the precautions already described must be observed. The precipitate with paper is ignited in a porcelain crucible at  $700^{\circ}$ - $800^{\circ}$  C., cooled and dissolved in 5-6 ml. dilute nitric acid of s.g. 1.2 and from this point the procedure is the same as already described.

The great advantage of this method lies in the fact that the solution of the oxide which results from the sulphide is much more rapid than the solution of the copper and the copper sulphide which latter is necessarily present when copper is precipitated by means of zinc and hydrogen sulphide water.

#### EXPERIMENT 60.

##### **Complete Analysis of Chrome-Iron-Ore.**

The following are determined :— $\text{Cr}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{FeO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$  and Loss on ignition.

##### **Determination of $\text{Cr}_2\text{O}_3$**

##### **Principle :—**

When the ore is fused in a nickel crucible at a dull red heat with sodium peroxide, the chromium in it is converted into sodium chromate, the  $\text{SiO}_2$  and the  $\text{Al}_2\text{O}_3$  into sodium silicate and aluminate respectively, the  $\text{FeO}$  into  $\text{Fe}_2\text{O}_3$ , and the calcium and magnesium being left in the form of their oxides. When the fused mass is

dissolved in water and the solution is filtered, all the above substances excepting  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{CaO}$  pass into the filtrate. This is acidified with  $\text{H}_2\text{SO}_4$ , excess of sodium peroxide which has been changed into  $\text{H}_2\text{O}_2$  by the addition of water, destroyed by boiling with a solution of  $\text{KMnO}_4$ , the precipitated  $\text{MnO}_2$  dissolved by adding  $\text{HCl}$  and the chromic acid solution thus obtained is titrated against a standard solution of  $\text{FeSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $6\text{H}_2\text{O}$ , potassium ferricyanide acting as an external indicator.

#### Procedure :—

Introduce about 2 gms. of  $\text{Na}_2\text{O}_2$  (2 spatulafuls) into a nickel crucible. Introduce into it 0.5 gm. of the finely powdered ore (at least-100 mesh) accurately weighed, cover with a layer of 4-5 gms. of  $\text{Na}_2\text{O}_2$ . Stir the mass with a glass rod. Brush off particles sticking to it into the crucible with a camel hair brush. (In winter there is no difficulty in doing this ; but in the monsoon months, the mass becomes sticky and the removal of particles sticking to the rod is difficult. In such a season, it is best not to mix the contents at all.) Cover the crucible with a lid and heat the contents over a low Bunsen flame so that the bottom of the crucible is just at a dull red heat. Maintain at this heat for 15 minutes. Cool. Add again 2 gms more of the peroxide and heat for 10 minutes more. Get a beaker (600 ml. capacity) containing about 300 ml. water ready by heating it to about  $80^\circ\text{C}$ . When the nickel crucible and contents have been kept in a fused condition for half an hour on the whole, remove from the flame by means of tongs, and let cool. When cold plunge into the water in the beaker. Lift it off the surface of the water and rinse it three or four times with

water. To the solution in the beaker add 100 ml. of water and boil for 10 minutes to decompose  $\text{H}_2\text{O}_2$ . Filter. Cool. To the cooled filtrate add conc.  $\text{H}_2\text{SO}_4$  to distinct acidity. Heat on the hot plate or over a mushroom top burner. When boiling, add, in drops, a 5%  $\text{KMnO}_4$  solution until a pink colour persists. When the boiling is continued for 15 minutes, introduce 10-15 ml.  $\text{HCl}$  of 1.1 s.g. Add 200 ml. more water. Continue boiling until the smell of chlorine is no longer perceptible. This will be the case when the volume has been reduced, by boiling, by about 100 ml. The solution must at this stage be perfectly clear. Cool. Finish by titrating with standard  $\text{FeSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $6\text{H}_2\text{O}$ . The procedure is the same as in determining Fe in an iron ore by using standard  $\text{K}_2\text{Cr}_2\text{O}_7$  for titration, except that in the former case, the standard ferrous sulphate solution is run from the burette whereas in the latter case, the standard dichromate is run into the reduced iron solution. A better way of carrying out the titration is to add excess of the standard ferrous ammonium sulphate solution and titrate the excess back with standard potassium dichromate solution. The volume of standard ferrous ammonium sulphate solution used up gives a measure of the amount of Cr in the ore.

### Determination of $\text{SiO}_2$ :—

#### Principle and Procedure :—

As given under the heading 'Principle' for  $\text{Cr}_2\text{O}_3$  determination, the  $\text{SiO}_2$  in the ore is converted into  $\text{Na}_2\text{SiO}_3$  on fusion with  $\text{Na}_2\text{O}_2$  in a nickel crucible. The fused mass is taken up in water in a 5 to 6 inch porcelain evaporating dish, treated with conc.  $\text{HCl}$  to distinct

acidity and evaporated to dryness. The dried mass is boiled with 50 ml. dil. HCl and the  $\text{SiO}_2$  filtered off, ignited and weighed. The  $\text{SiO}_2$  may be purified by treatment with  $\text{H}_2\text{SO}_4$  and HF when a high degree of accuracy is required.

### Determination of FeO :—

To the filtrate from  $\text{SiO}_2$ , add 3 gms.  $\text{NH}_4\text{Cl}$  and then ammonia until it smells of it. Boil. Filter off the mixed precipitates of  $\text{Fe}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$  and  $\text{Cr}(\text{OH})_3$ . Redissolve in dil. HCl (1 : 1) and reprecipitate by the addition of ammonia, filter off the precipitate, dissolve in dil HCl, reduce when hot with  $\text{SnCl}_2$ , cool, add  $\text{HgCl}_2$  to remove excess of  $\text{SnCl}_2$  and titrate with standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution, using  $\text{K}_4\text{FeCy}_6$  as an external indicator. See Expt. 10.

### Determination of $\text{Al}_2\text{O}_3$ :—

Extract the fusion product of 1 gm. ore with  $\text{Na}_2\text{O}_2$  with water. Bring the volume of solution to about 300 ml. Boil to decompose excess  $\text{Na}_2\text{O}_2$ . Filter. To the filtrate which contains Al as  $\text{NaAlO}_2$  and Cr as  $\text{Na}_2\text{CrO}_4$  add dil. HCl until faintly acid. Add excess of  $(\text{NH}_4)_2\text{HPO}_4$  solution to precipitate Al as  $\text{AlPO}_4$  and 5 gms. of  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  to convert any free HCl into  $\text{C}_2\text{H}_3\text{O}_2$  and thereby destroy the solvent action of HCl on  $\text{AlPO}_4$ . Boil, filter off the precipitate of  $\text{AlPO}_4$ , ignite in a porcelain crucible and weigh.

### Determination of CaO and MgO :—

The following is the scheme in outline for the determination of CaO and MgO :—

Fuse the ore with  $\text{Na}_2\text{O}_2$ , dissolve in water and filter.

Residue consists of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{CaO}$ ,  $\text{MgO}$  and  $\text{NiO}$  (the last from the nickel crucible in which fusion is effected). Dissolve in  $\text{HCl}$  and start evaporation.

Filtrate consists of  $\text{Na}_2\text{CrO}_4$ ,  $\text{Na}_2\text{SiO}_3$ ,  $\text{NaAlO}_2$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_3\text{PO}_4$ .

Add  $\text{NH}_4\text{Cl}$  until fixed alkali is destroyed, boil and filter.

Residue consists of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{AlPO}_4$ . Dissolve in  $\text{HCl}$ .

Filtrate consists of  $\text{Na}_2\text{CrO}_4$ ,  $\text{Na}_2\text{SO}_4$ .

Mix the two solutions and continue evaporation to dryness. Redissolve in dil.  $\text{HCl}$  and filter.

Residue is  $\text{SiO}_2$ .

Filtrate consists of  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{MnCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$  and  $\text{H}_3\text{PO}_4$ . Throw down  $\text{Fe}$  and  $\text{Al}$  as phosphates and as basic acetates and filter.

Filtrate consists of the salts of  $\text{Mn}$ ,  $\text{Ca}$  and  $\text{Mg}$ . Add ammonium persulphate and ammonium hydroxide. Boil filter.

Residue consists of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ .

Residue is  $\text{MnO}_2$ .

Filtrate consists of salts of  $\text{Ni}$ ,  $\text{Ca}$  and  $\text{Mg}$ . Pass  $\text{H}_2\text{S}$  and filter.

Residue is  $\text{NiS}$ .

Filtrate consists of salts of  $\text{Ca}$  and  $\text{Mg}$ . Proceed as in Expt. 11.

### Procedure :—

Fuse 0.5 gm. sample of the ore with  $\text{Na}_2\text{O}_2$  as in the determination of  $\text{Cr}$  and proceed exactly as shown thereunder until the residue is separated from the soluble



chromate, silicate and aluminate and small amounts of sodium sulphate and phosphate. Wash the residue with water until the filtrate is free from chromate. Dissolve the residue in dil. HCl (1 : 1) and evaporate in the dish. When this is evaporating, proceed with the filtrate by boiling it after the addition of 1.5-2.0 gms. of  $\text{NH}_4\text{Cl}$ . Boil to a faint smell of ammonia and filter. Wash until filtrate runs colorless. A check on the chromium determination may, if desired, be made on the filtrate. Dissolve the residue in 15 ml. of 1 : 1 HCl and add to the solution that is already evaporating. Evaporate to dryness and bake at a temperature not exceeding  $130^\circ\text{C}$ . Cool. Redissolve in 30ml. dil. HCl and filter. Wash residue with hot water 5 or 6 times. Proceed with filtrate as in Expt. 21 for throwing down Fe and Al as basic acetates and phosphates. Filter. Wash 3 or 4 times with water. Determine Al from the residue by dissolving it in HCl and precipitating it as  $\text{AlPO}_4$ , after the addition of  $\text{Na}_2\text{HPO}_4$ ,  $\text{Na}_2\text{S}_2\text{O}_8$  and  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ . Throw down Ni from the filtrate from the basic acetate separation by passing  $\text{H}_2\text{S}$ . Filter. Wash with  $\text{H}_2\text{S}$  water containing a little ammonium acetate. Determine Ca from the filtrate by adding  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  and finishing as in Expt. 11. Evaporate filtrate from  $\text{CaC}_2\text{O}_4$  to dryness in a casserole. Heat to destroy ammonium salts. Cool. Dissolve residues in 5 ml. of 1 : 1 HCl and dilute to about 15 ml. with water. Throw down Mg as  $\text{MgNH}_4\text{PO}_4$ , let stand for about 12 hrs., filter, wash with 1 : 10  $\text{NH}_4\text{OH}$ , dry the precipitate and ignite it in a porcelain crucible, gently at first and strongly afterwards. Cool. Weigh as  $\text{Mg}_3\text{P}_2\text{O}_7$ .

#### Loss on Ignition :—

Heat 1 gm. of the sample in a platinum crucible covered with lid over a blast lamp for  $\frac{1}{2}$  hour. Cool in a desiccator and weigh.

## NOTES :—

(1) The fusion process adopted here is known as oxidising fusion. A mixture of  $\text{Na}_2\text{CO}_3$  with a small quantity of  $\text{KNO}_3$  may be substituted for  $\text{Na}_2\text{O}_2$  and the fusion of the ore with such a mixture effected in a platinum crucible. But the use of a nickel crucible with  $\text{Na}_2\text{O}_2$  as the oxidising agent is preferable in as much as platinum vessels are not pressed into service where they can be dispensed with.

(2) The heat for fusion must be a dull red heat only ; otherwise the life of the nickel crucible is shortened.

(3) (a) Dilution with water of the extract of the fusion to the specified volume is necessary ; otherwise the strongly alkaline solution will attack the filter paper during the subsequent filtration. The addition of 2-3 gms. of ammonium carbonate to the fusion extract will obviate the necessity for large dilution. The filtration can, in that case, be carried out quicker.

(b) Acidified solution of sodium or other chromate is reduced by  $\text{H}_2\text{O}_2$ . Therefore the latter should be expelled from a chromate solution before it is acidified. As it is difficult to expel  $\text{H}_2\text{O}_2$  completely from alkaline solutions containing chromate, as much of it as possible is expelled by boiling, the solution then acidified and any chromium salt formed from the chromate by the action of traces of  $\text{H}_2\text{O}_2$  oxidised back to the chromate by adding  $\text{KMnO}_4$ , the excess of this being destroyed by  $\text{HCl}$ . The latter when present in the dilution specified has no reducing action on  $\text{CrO}_3$  even when the two are boiled.

(4) Before proceeding with the determination for any of the constituents, it is necessary to ascertain that all the ore has been attacked by the fusion. The only means of doing this is to dissolve the residue on the

filter in warm dil. HCl. If it dissolves completely the fusion is perfect ; if it does not, the insoluble portion, washed free of acid, should be ignited in the same nickel crucible and again fused with half the quantity of  $\text{Na}_2\text{O}_2$  used at the start. The extract of the second fusion must be filtered and added to the one obtained from the first fusion.

(5) The determination of Fe should be carried out as described. Interference is caused by the presence of nickel taken up from the crucible during the fusion, when the solution of the residue in HCl is reduced by means of  $\text{SnCl}_2$  and the reduced solution, after the addition of  $\text{HgCl}_2$  is titrated with standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution, using potassium ferricyanide as the external indicator.

(6) If the results of analysis are not required urgently, the following alternative method may be substituted for the determination of  $\text{Al}_2\text{O}_3$  :—

Pass a current of  $\text{CO}_2$  from a Kipp's apparatus through the alkaline chromate solution for a period of about 12 hours. Al is precipitated as a basic carbonate. This is filtered off, ignited and weighed as  $\text{Al}_2\text{O}_3$ .

(7) In case the ore contains any titanium, this will be found as sodium meta titanate in the residue obtained by filtering off the solution in water following the peroxide fusion attack. This will accompany aluminium through all the steps in the process. An accurate determination of aluminium and titanium may be made as in Expt. 67. For the purposes for which the ore is used, such refinement in analysis is seldom called for.

(8) Chrome iron ore is used largely in the manufacture of ferrochrome, chrome bricks and in the tanning of leather. For the last use the ore has to be converted into sodium or potassium dichromate.

## EXPERIMENT 61.

**Analysis of Bauxite :—**

The material should be ground to pass a 90 mesh sieve. It is freed from moisture by heating in an air oven at 105 to 110°C. to constant weight.

**Loss on Ignition :—**

Ignite 1 gm. of the moisture-free sample in a platinum crucible covered with lid for 1 hour over a blast lamp or a muffle furnace. The loss in weight represents the loss on ignition.

Determination of  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{MnO}$ :—

**Outline of Procedure :—**

The sample of ore is opened out by a fusion attack with sodium carbonate, the fused mass being extracted with sulphuric acid, after it has solidified and cooled to room temperature. The solution is evaporated to fumes of  $\text{SO}_3$  and redissolved in water and filtered. The residue is hydrofluorised. Any residue left from the hydrofluorisation treatment is fused with  $\text{KHSO}_4$ , extracted with  $\text{H}_2\text{SO}_4$  and the solution added to the main filtrate. From this  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{CaO}$  and  $\text{MgO}$  are determined.

**Silica :—**

Fuse the ignited residue with 10 gms. of 'fusion mixture' in a platinum crucible over a Teclu burner for 30 minutes. Extract with 150-200 ml. of  $\text{H}_2\text{SO}_4$  (1:9) and evaporate to fumes of  $\text{SO}_3$ . Cool. Add 100-150 ml. of water, heat for 10 minutes and filter. Receive filtrate in a 500 ml. measuring flask, wash residue on the paper with dil.  $\text{HCl}$  (1:2) and finally with hot water. Ignite the residue in a platinum crucible, cool and weigh. Treat with water,  $\text{H}_2\text{SO}_4$  and  $\text{HF}$ , Ignite, cool and weigh. The loss represents  $\text{SiO}_2$ .

Fuse any residue left in the crucible with  $\text{NaHSO}_4$ , extract with dil.  $\text{H}_2\text{SO}_4$  (1:5) and add to the main filtrate in the 500 ml. measuring flask. Cool. Make up to the mark with dil.  $\text{H}_2\text{SO}_4$  (1:9). Use aliquot parts from this for the following determinations:  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{CaO}$  and  $\text{MgO}$ .

**$\text{Fe}_2\text{O}_3$  :—**

Pipette off 50 ml. into a 200 ml. beaker and determine  $\text{Fe}_2\text{O}_3$  from this as in Expt. 10.

**$\text{TiO}_2$  :—**

Pipette off 10 ml. into a colour comparison tube. Dilute with 10 ml. of dil.  $\text{H}_2\text{SO}_4$  of s.g. 1.04. Add 2-3 ml. of hydrogen peroxide. Determine colorimetrically as shown in Expt. 37.

**$\text{Al}_2\text{O}_3$  :—**

Pipette off 100 ml. from the measuring flask into a 600 ml. beaker. Dilute to 350-400 ml. with water. Add ammonia until alkaline. Use a few drops of methyl red to indicate the alkalinity. The appearance of a yellow colour marks this point. The yellow colour is easily observed by allowing the precipitate to settle. Boil. Filter off the hydroxides, wash, dry, ignite, cool and weigh. This represents the weight of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ . From this subtract the sum of the weights of  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ . The difference yields the weight of  $\text{Al}_2\text{O}_3$ . In obtaining by difference the weight of  $\text{Al}_2\text{O}_3$ , regard should be had to the weights that the aliquot parts for  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  determinations represent.

**$\text{MnO}$  :—**

To the filtrate from  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{TiO}_2$ , add bromine water and then ammonia until alkaline. Boil. Filter off  $\text{MnO}_2$ , ignite in a porcelain crucible in a muffle furnace to  $\text{Mn}_3\text{O}_4$  and weigh. Calculate to  $\text{MnO}$ .

### CaO and MgO :—

Determine these from the filtrate from MnO in the manner shown in Experiment 11, after evaporation to dryness, destruction of ammonium salts by heating, and solution of residues in 5 ml. of dil HCl (1:1)

### Alkalies :—

Determine by the method of Lawrence Smith. See Expt. 77.

### NOTES :—

(1) On account of the presence of high percentages of titania in some samples of bauxite and on account of the fact that titanium tetrachloride is appreciably volatile, evaporation of the fused mass with  $\text{H}_2\text{SO}_4$  in place of HCl is preferred. Also, the  $\text{SiO}_2$  is more easily filtered off in this case than when using HCl.

(2) When a high degree of accuracy is desired, iron may be separated as FeS by the method of Gooch by precipitating it as FeS in ammonium sulphide-tartrate solution, filtering it off, igniting to oxide, dissolving in HCl, and completing the determination as in Expt. 10.

(3) In case large amounts of titanium are present, it may be precipitated from the filtrate obtained by filtering off FeS (which has been thrown down according to the method of Gooch) by means of the cupferron reagent. See Expt. 37-A. The precipitate is filtered off, washed with 2N-HCl followed by water, ignited slowly and then strongly and then weighed as  $\text{TiO}_2$ .

The filtrate from the cupferron precipitation of titanium may be used for a direct determination of aluminium in the manner shown in Expt. 56, Notes, para 5. The only objection to the use of cupferron in the routine analysis of bauxite is that it is costly and sufficiently accurate results for commercial purposes can be obtained by calculating the % of aluminium from the

weight of the mixed oxides consisting of  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$ , which oxides are thrown down by the ordinary reagent  $\text{NH}_4\text{OH}$ .

(5) A more accurate procedure for  $\text{CaO}$  and  $\text{MgO}$  consists in throwing them down as oxides by means of  $\text{NaOH}$ .  $\text{Fe}$  and  $\text{Ti}$  are coprecipitated.  $\text{Al}$  remains in solution as  $\text{NaAlO}_2$ . The precipitate is dissolved in  $\text{HCl}$ ,  $\text{Fe}$  and  $\text{Ti}$  precipitated by  $\text{NH}_4\text{OH}$ , the precipitate filtered off and  $\text{CaO}$  and  $\text{MgO}$  determined from the filtrate as in Expt. 11. The procedure is as follows :—

1 gm. sample of moisture-free bauxite is fused with 10 gms. of fusion mixture and the melt treated as shown under 'Silica' determination above until a silica-free filtrate is obtained. The free acid is neutralised, the solution is poured into 150 ml. of  $\text{NaOH}$  solution (10%) containing one gm. of  $\text{Na}_2\text{CO}_3$  and kept simmering by heating on a steam-bath for half an hour. This is then filtered and the precipitate washed with 1%  $\text{Na}_2\text{CO}_3$  solution. The residue is dissolved in 25 ml. of 1:1  $\text{HCl}$  and precipitated by the addition of  $\text{NH}_4\text{OH}$  until the methyl red indicator shows a yellow colour. The precipitate of  $\text{Fe}(\text{OH})_3$  may cause some difficulty in catching the point at which the liquid is yellow. If the precipitate is allowed to settle and then the colour looked for, there will be no difficulty. Filter off the precipitate, dissolve it in  $\text{HCl}$  and repeat the precipitation with  $\text{NH}_4\text{OH}$  using methyl red indicator to indicate the point at which the medium is just ammoniacal. Combine the filtrates from the two precipitations and proceed for the determination of  $\text{CaO}$  and  $\text{MgO}$ . See Expt. 11.

(9) Instead of a fusion attack, the material may be opened out with a mixture of sulphuric, nitric and hydrofluoric acids. The only drawback to this method is that a silica determination is not possible. But where

it is the commercial valuation of the ore, quick results for  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  can be obtained by the acid attack.

### EXPERIMENT 62 A.

#### Complete Analysis of Zinc Blende.

Determination of 'Insoluble', Pb, Cu, Cd, Fe, Mn., Zn, S and  $\text{CO}_2$

##### Insoluble Matter :—

Weigh 1 to 1.5 gms. sample in a 200 ml. tall form beaker. Add 5 ml. of water and 20 ml. of conc. hydrochloric acid. Warm on the hot plate or on a sand bath and add in small quantities at a time 5 ml. of conc. nitric acid. When the ore is in solution except for the insoluble matter, add 10 ml. more of dil. HCl s. g. 1.1 and boil for 5 minutes. Filter the hot solution through a 7 cm. filter-paper and wash the residue on the paper with boiling hot hydrochloric acid of s. g. 1.1. This wash will dissolve any lead sulphate which is on the paper. Wash next with water. Ignite and weigh. Calculate % 'Insoluble'.

##### Lead :—

Evaporate the filtrate to about 10 ml. Cool, add 3 ml. of conc. sulphuric acid and evaporate on a sand-bath until dense fumes of sulphur tri-oxide are evolved. Cool. Dilute with water to about 100 ml. Filter through a Gooch crucible. Wash with normal sulphuric acid and then with alcohol. Ignite the ppte. by placing the Gooch crucible inside an ordinary crucible. Cool and weigh. See Expt. 62 C. Alcohol washings are to be rejected.

##### Copper :—

Evaporate the filtrate and washings from the lead sulphate until fumes of sulphuric acid are evolved. Cool. Add 20 ml. water and 20 ml. conc. HCl. Heat to



boiling. Pass a current of  $H_2S$  until the solution is cold. Filter. Wash with a mixture of equal volumes of conc.  $HCl$  and saturated hydrogen sulphide solution. Reserve filtrate for cadmium determination.

Dissolve the ppte., if small, in conc.  $HNO_3$ . If it is bulky, ignite to oxide and then dissolve in conc.  $HNO_3$ . Add ammonia, boil, and then add acetic acid. Cool. Add  $KI$  (2-3 gms). Titrate the iodine liberated with standard sodium thiosulphate solution. See Expt. 59.

#### **Cadmium :—**

Evaporate the filtrate from  $CuS$  to fuming. Cool. Add 5 ml. conc.  $HCl$  and transfer the solution to a conical flask, using  $H_2S$  soln. to rinse the basin. Then add slowly and with constant stirring  $H_2S$  solution until the volume is increased to about 150 ml. Saturate the solution with  $H_2S$ . Filter. Wash with 5%  $NH_4NO_3$  soln. Dissolve the ppte. in the minimum amount of conc.  $HCl$ , wash the filter with hot dil. acid and transfer the filtrate and washings to a large size porcelain crucible. Add 0.5 ml. conc.  $H_2SO_4$  and evaporate to fumes. Heat inside a larger crucible to expel the fumes of  $SO_3$ . Temperature should not exceed  $600^\circ C$ . Weigh as  $CdSO_4$ .

#### **Iron :—**

Evaporate the filtrate from the cadmium sulphide to about 50 ml. Transfer to a beaker, add 1 ml. of conc.  $HNO_3$ , boil to oxidise ferrous to ferric salt and dilute to 100 ml. Add ammonium chloride (2 gms) and excess of ammonia. Boil. Filter. Call the filtrate F. Redissolve the ppte. in dil.  $HCl$  and reprecipitate by  $NH_4OH$ . Filter, adding the filtrate to filtrate F. Wash the ppte. with water. Ignite and weigh as  $Fe_2O_3$ .

#### **Manganese :—**

Evaporate the combined filtrate F after the addition

of 2-3 ml. conc.  $\text{H}_2\text{SO}_4$  to fumes. Dilute to 200 ml. with water. Add 2 gms. of ammonium persulphate dissolved in 50 ml. of water and raise to a boil. Neutralise with ammonia until faintly ammoniacal. Boil for two minutes and filter through a filter paper of 7 cm. dia. Ignite at a temp. of  $800-950^\circ\text{C}$ . in a muffle furnace. Cool and weigh as  $\text{Mn}_2\text{O}_3$ .

### **Zinc :—**

Make up the filtrate to 500 ml. in a graduated flask. Mix thoroughly. Determine the zinc on an aliquot part of the filtrate as zinc ammonium phosphate. See Expt. 41. Filter. Ignite and weigh as zinc pyrophosphate or determine volumetrically using standard potassium ferrocyanide soln. for titration and uranyl acetate as external indicator. See Expt. 41, p. 219. Alternatively 0.1 gm diphenylamine dissolved in 10 ml. of conc.  $\text{H}_2\text{SO}_4$  may be used as internal indicator. A few drops of the indicator soln. will do. Change from purple violet to pea-green marks the end.

### **Solution Required :—**

Dissolve 28 gms. of  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  in about 900 ml. water. Add 0.3 gm  $\text{K}_3\text{Fe}(\text{CN})_6$  and make up to one litre. This solution is approximately fifth normal.

### **Standard Zinc Sulphate Solution :—**

Dissolve 7.189 gms of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in water and make up to 250 ml. in a measuring flask.

### **Standardization of the Pot. Ferrocyanide Solution :—**

Pipette off 25 ml. of the zinc sulphate soln. into a 400 ml. beaker. Add 20 ml.  $4N-\text{H}_2\text{SO}_4$ , 5—10 gms of  $(\text{NH}_4)_2\text{SO}_4$  and 50 ml. of water. Add 3 drops only of the indicator and run in the ferrocyanide from a burette. The blue-violet colour changes on standing.

## EXPERIMENT 62 B.

**Determination of Tin in Tin Ore :**

The chief ore of tin is cassiterite. It has the formula  $\text{SnO}_2$ . This is insoluble in all acids.

**Principle :—**

The finely powdered ore ( -100-mesh ) on fusion with sodium peroxide yields sodium stannate. This is dissolved in HCl and the stannic chloride obtained is reduced with iron or nickel to stannous chloride. The reduced solution is oxidized to stannic chloride with standard iodine solution, starch being used as indicator. The volume of the iodine solution used is a measure of the amount of tin in the ore. The main reaction on fusion is as follows :—



The solutions required and the method of standardisation are shown at the end of this exercise.

**Procedure :—**

Place about 2 to 3 gms. of sodium peroxide in a nickel crucible. The peroxide should be removed by a dry nickel spatula from the reagent bottle. It should not be weighed on bits of paper. Weigh on a watch-glass. The reagent is very corrosive. Wash spatula with water. Do not wipe with duster after letting it stand in the air for some time after the removal of the peroxide from the Reagent bottle. Weigh 0.5 gm. sample of the tin ore into the crucible. Cover the ore with about 1 gm. more of the peroxide. Heat gently over a Bunsen burner and then strongly until the fusion is quiescent. The fusion is better effected by giving the crucible a rotatory motion all the time ( about 10–15 minutes ) the operation is in progress. Seize the hot crucible by means of a pair of steel tongs and slightly rotate the crucible so that the melt adheres

all round its side. Place about 200 ml. of hot water in a 400 ml. beaker and cautiously introduce the cold nickel crucible with its contents into it. Plunging it into the water all at once causes a brisk effervescence which may overflow the beaker. Wash the crucible with hot water, rub with a policeman and transfer residue and liquid in the crucible to the beaker. A few drops of dilute HCl may be added to the crucible to remove any residue not removed by water. Transfer the solution in the beaker to a 600 ml. flask. The volume of the liquid, only water being used to rinse the beaker, must be about 300 ml. Add 100 ml. conc. HCl to the flask. Fit the flask with a Bunsen valve. See Fig. 9. Introduce sheet nickel strips having an area of about 100 sq. cms., bent at the corners, into the flask and a small piece of calcite. Set up as shown in Fig. 9 with the Bunsen valve and heat for  $1\frac{1}{2}$  to 2 hours on the hot plate or over a Bunsen burner gently. At the end of this time, the reduction is complete. The flask is cooled, the contents diluted with 100 ml. water and then titrated with standard iodine solution and starch, prepared as described below, until a blue colour is obtained.

An iron crucible may be used in place of a nickel crucible for carrying out the fusion of the ore.

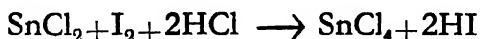
2-3 gms. of mild steel drillings may be substituted for nickel strips. The excess need not be removed before titration.

Granulated lead may with advantage be substituted for nickel, as the end point in the titration process can be more easily seen.

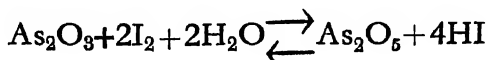
If, in a determination, 20.0 ml. of iodine solution, 1 ml. of which = 0.005 gm. Sn, are required, the percentage of tin in the ore is 20, starting with 0.5 gm. of the ore. . .

### Preparation of Standard Iodine Solution :—

The reaction that takes place when iodine solution is run into stannous chloride is represented as follows:—



1 gm.-atom of iodine in 1 litre of water yields a normal solution. The use of a solution 1 ml. of which corresponds to 0.005 gm. tin is convenient inasmuch as the calculations are thereby rendered easy. 11 gms. of iodine are dissolved in a strong solution of 22 gms. KI in water and the solution then diluted to 1 litre. The iodine solution is standardised against pure  $\text{As}_2\text{O}_3$ . The reaction that takes place when iodine acts on  $\text{As}_2\text{O}_3$  is represented by the following equation :—



The conditions necessary to effect the change indicated by the upper arrow quantitatively are that  $\text{As}_2\text{O}_3$  must be in solution and that there should be in the solution an excess of bicarbonate of sodium to remove the hydriodic acid formed.

### Preparation of $\text{As}_2\text{O}_3$ solution and Procedure for Stanardisation :—

Weigh 0.3000 gm. of  $\text{As}_2\text{O}_3$  exactly in a 100 ml. beaker. Add 5 to 8 ml. of a 10% solution of sodium hydroxide in water and heat gently to effect solution. When dissolved, make faintly acid with hydrochloric acid, testing by dropping a piece of litmus paper. Transfer to a 400 ml. beaker. Dilute with cold water to about 200 ml. Add an excess of solid sodium bicarbonate. The excess is indicated by the cessation of effervescence and by some solid remaining undissolved at the bottom of the beaker. Add 3 ml. of starch indicator prepared as in Expt. 19. Next run the iodine solution from a burette into the

solution of arsenite until a blue colour is obtained. Calculate the normality of the iodine solution and hence its value per ml. in terms of tin. See Example towards the end of this exercise. The standardisation may also be effected with pure tin which is dissolved in conc. HCl. The solution obtained is reduced by means of nickel exactly as in the assay of the ore and the titration with iodine carried out. This method is rather slow. Hence, preference to the method first described.

### Notes on the assay :—

(1) The presence of arsenic, titanium and tungsten in the ore interferes with the assay. The first of these elements is changed to arsenate by fusion with  $\text{Na}_2\text{O}_2$ . In the presence of HCl and Ni, it is reduced to  $\text{H}_3\text{AsO}_3$ . This, on treatment with iodine solution passes to the condition of  $\text{H}_3\text{AsO}_4$ . Thus, the value returned for tin will be high. But this oxidation by iodine can be and is prevented by the addition of a very liberal amount of HCl at the very outset of the reduction by nickel. In the presence of a strong acid medium, the oxidation of arsenious acid to arsenic acid does not take place.

(2) For a qualitative test for Ti, see Experiment 56. Titanium gives rise to  $\text{TiCl}_4$  and  $\text{TiCl}_3$ . The former is obtained on the addition of acid to the alkaline fusion. Ni reduces  $\text{TiCl}_4$  to  $\text{TiCl}_3$ . The solution of iodine oxidises  $\text{TiCl}_3$  to  $\text{TiCl}_4$ ; but this oxidation is not quantitative; hence the determination of Ti and allowance for it is not possible. Recourse must, therefore, be had to fusion with potassium bisulphate in a platinum crucible. The tin oxide is unaffected by this fusion; but all the titanium and the tungsten in the ore are changed to  $\text{Ti}(\text{SO}_4)_2$  and  $\text{WO}_3$ . The fused mass is digested with 20-30 ml. warm dil. sulphuric acid

(1 : 5), filtered and washed first with water and then with ammonium carbonate solution.  $(\text{NH}_4)_2\text{CO}_3$  wash removes any tungstic acid that may be present with the residue. If the percentage of tungsten in the ore is required, proceed, by acidifying the filtrate with hydrochloric acid and adding cinchonine hydrochloride. See Expt. 31, p. 168. The residue on the filter paper consists of  $\text{SnO}_2$  and impurities like  $\text{SiO}_2$ ,  $\text{CaSO}_4$  etc. which do not interfere with the determination of using standard iodine solution. It is ignited in a nickel crucible and the fusion with  $\text{Na}_2\text{O}_2$  is then adopted.

(3) The presence of tungsten is revealed by a blue precipitate appearing after reduction with nickel, when the peroxide fusion is adopted. This is filtered off, the filtrate again reduced with nickel and the titration completed as described. Perform the following test for the presence of tungsten in a tin ore :—Fuse about 0.1 gm. ore with 1 gm.  $\text{Na}_2\text{O}_2$  in a silver crucible. Extract with water. Add to a part of the solution 3-5 ml. conc.  $\text{HCl}$  and a few bits of metallic tin. A blue colour appearing after 2-3 minutes reveals the presence of tungsten. The use of a silver crucible in preference to a nickel crucible is to avoid the colour resulting from the solution of nickel in  $\text{HCl}$ . The green colour of nickel salts tends to mask the blue of  $\text{W}_5\text{O}_{15}$ .

(4) The effect of atmospheric oxidation on the solution of  $\text{SnCl}_2$  is considerable. Hence arises the necessity for carrying out the reduction by means of nickel out of contact with air. The titration too should be carried out in an atmosphere of  $\text{CO}_2$  at a temp. of  $70^\circ\text{F}$ . or below and after diluting with water. This may be achieved by the introduction of a small piece of pure calcite (Iceland spar) into the solution ready for titration. Carry out the titration after all the calcite has dissolved. Alternatively a

current of  $\text{CO}_2$  may be passed into the flask during the titration. It is difficult to catch the blue colour of iodide of starch, if the liquid is not largely diluted. The water used must be recently boiled and cooled. Only such water will be free from dissolved oxygen and will not have an oxidising action on the stannous chloride.

**Dry Assay :—** The method described above is known as the 'Wet Assay' of tin. Where elaborate equipment is not available, recourse may be had to the dry assay of tin which gives results of fair accuracy. The dry assay is performed as follows :—

Crush the ore to pass an 80-mesh sieve, and weigh out the following charge into a fire-clay crucible, ( size D or E ).

Ore	10 gms
Potassium cyanide	40 gms

Common commercial cyanide containing 50% carbonate is most suitable. Place part of the cyanide at the bottom of the fireclay crucible. Mix the remainder with the ore on a glazed paper and then transfer to the crucible. Heat it in a wind-furnace until the charge is thoroughly fused and then raise the temperature to  $1000^\circ\text{C}$ . for a few minutes and pour the melt into an iron mould. The reduction takes about 20 minutes. When the slag is completely solidified and cold, detach by hammering it off, clean and weigh the tin button. Compare with the wet assay results.

**NOTE :—**

Potassium cyanide is a deadly poison. It decomposes in moist weather forming hydrocyanic acid. This acid is volatile. The acid when inhaled will have a fatal effect. Therefore the operation of weighing, mixing, etc. of the charge for fusion



should be conducted in well ventilated rooms. The instructions re : treatment for cyanide poisoning are given below :—

### Antidote for cyanide poisoning (Matrin's Antidote)

( Dr. Martin was appointed in 1902 by the Australian Govt. to report on antidotes for poisoning. His antidote has been universally acknowledged to be the safest and most reliable corrective ).

The ingredients for one treatment are provided in the following form :—

A. A hermetically sealed glass tube containing  $7\frac{1}{2}$  gms.  $\text{FeSO}_4$  and 30 ml. water.

B. A hermetically sealed glass tube containing  $1\frac{1}{2}$  gms.  $\text{NaOH}$  in 30 ml. water.

C. A tube containing 2 gms powdered magnesia. A and B are broken into an enamelled iron mug, C being added then and the whole well stirred. The mixture is then drunk, the strainer mouthpiece of the mug prevents broken glass being swallowed. In case the patient cannot drink, a mouth gag and stomach tube are inserted and the antidote poured down.

An injection of **adrenaline** delays the fatal effect of the poison and gives time for the preparation of the antidote.

**Example :—**

0.3000 gm. of  $\text{As}_2\text{O}_3$  consumed 65.0 ml. I-solution.

$\frac{197.92}{4}$  gms. of  $\text{As}_2\text{O}_3$  in 1 litre yield N-soln.

0.3 gm. of  $\text{As}_2\text{O}_3$  in 1 litre yields  $\frac{0.3 \times 4}{197.9}$  N-soln. .

1 litre of  $\text{As}_2\text{O}_3$  solution of  $\frac{0.3 \times 4}{197.9}$  N-strength is equivalent to 65.0 ml. of I solution.

Therefore, strength of the I-soln. =  $\frac{1.2 \times 1000}{197.9 \times 65} N = 0.0933 N$

1 litre N-Iodine soln. =  $\frac{118.7}{2}$  gms. Sn.

1 ml. of 0.0933 N soln. = 0.00554 gm. Sn.

Weight of ore taken = 0.5100 gm.

Number of ml. of the standard I soln. used up = 66.0

Amount of tin in the weight of ore taken =  $66 \times 0.00554$  gm.

100 gms. ore contain  $\frac{66 \times 0.00554 \times 100}{0.51}$  gm. Sn.

Percentage of Sn in the ore 71.7

NOTE :—

The sample of ore analysed is a hand picked specimen from Tavoy, Burma, and contains tungsten.

## EXPERIMENT 62.C

### Determination of Tin in an ore (Alternative Method). Absence of Titanium and Tungsten

#### Principle :—

When to a solution of sodium stannate acidified strongly with HCl, iron filings are added and the solution heated to about 60°C., any As, Sb, Cu present is deposited as metal and the stannic chloride is reduced to the stannous condition. The deposit is filtered off, and the filtrate treated with pure zinc. Tin is deposited on the pieces of zinc. These are filtered off and dissolved in hot HCl in a flask through which CO<sub>2</sub> is being passed. When all the metal is in solution, it is cooled to the laboratory temperature, CO<sub>2</sub> current being maintained all the time. The cold solution is then titrated with standard iodine solution, using starch as indicator.

#### Procedure :—

Proceed as described in Experiment 26B until HCl

solution of the fusion is obtained. Add 4 gms. of iron filings and heat to about  $60^{\circ}\text{C}$ . After about half an hour, filter through a 10 cm. filter paper, catching the filtrate in a 500 ml. Erlenmeyer flask. Add 10 gms. of pure zinc to the contents of the flask and heat to about  $90^{\circ}\text{--}95^{\circ}\text{C}$ . for 10 minutes. Withdraw a few drops from the flask, place them on the spotting plate, and treat with a few drops of  $\text{H}_2\text{S}$  water. A black coloration shows that all the tin has not been deposited. Continue heating until the test shows no tin to be in solution. Filter off the deposit of tin through glass wool. Transfer to an Erlenmeyer flask the deposit of tin with the glass wool and treat with 30 ml. conc.  $\text{HCl}$ . Pass  $\text{CO}_2$  from a Kipp generator and warm the flask to hasten solution. When dissolved, cool the flask to room temperature, maintaining  $\text{CO}_2$  current all the time. Dilute to about 250 ml. with recently boiled and cooled distilled water and titrate with standard iodine solution.

**Example :—**

Weight of ore = 0.2023 gms.

Volume of I-soln. used to oxidise  $\text{SnCl}_2 = 14.4$  ml.

Weight of  $\text{As}_2\text{O}_3$  taken to standardise the iodine solution = 0.2 gm.

Number of ml. of iodine soln. used up. = 67.2 „

Hence, the strength of the iodine soln. = 0.0902 N

1 ml. of 0.0902 I soln. = 0.005365 N gm. Sn.

14.4 „ „ „ =  $14.4 \times 0.005365$  gm. Sn.

0.2023 gm. ore contains „ „ gm. Sn.

100 gms „  $\frac{100 \times 14.4 \times 0.005365}{0.2023}$  gm. Sn.

i. e. . 31.19% Sn.

## EXPERIMENT 62D.

**Determination of Pb in A Sulphide Ore.****Principle :—**

The ore is brought into solution in a mixture of HCl and  $\text{HNO}_3$  and the solution heated to fuming with  $\text{H}_2\text{SO}_4$ . The precipitated  $\text{PbSO}_4$  is impure and may contain  $\text{BaSO}_4$  and  $\text{SiO}_2$ . It is purified by treatment with ammonium acetate. Only the sulphate of lead is dissolved.  $\text{BaSO}_4$  and  $\text{SiO}_2$  remain unaffected. These are filtered off and from the filtrate lead is thrown down as  $\text{PbSO}_4$  by  $\text{H}_2\text{SO}_4$ . The precipitate is collected on asbestos filter in a Gooch crucible, ignited and weighed. From the weight of  $\text{PbSO}_4$ , the percentage of Pb is calculated.

**Solutions required :—**

1. Dilute  $\text{H}_2\text{SO}_4$ . Into 180 ml. water in a beaker, pour 20 ml. conc.  $\text{H}_2\text{SO}_4$ .
2. A saturated solution of ammonium acetate.

**Procedure :—**

Weigh 0.5 gm. sample of ore into a 200 ml. Jena flask. Add 10 ml. conc. HCl. Heat gently for 10 minutes. Add 5 ml. conc.  $\text{HNO}_3$ . Heat until nitrous fumes are expelled. Add 5 ml. more conc. HCl, boil for five minutes. Dilute to 50 ml., introduce 5 ml. conc.  $\text{H}_2\text{SO}_4$ , a little at a time. Heat until dense white fumes are evolved. Cool. Add 30 ml. of water. Boil. Let stand. Filter and wash the precipitate by decantation with solution No. 1 until the filtrate is free from iron (Test with KCNS solution).

Add 3 gms solid ammonium acetate to the flask containing the precipitate. Pour 10 ml. of solution No. 2 through the filter paper to dissolve any sulphate that may remain there and collect the solution in the

same flask. Heat to dissolve the lead sulphate. Any residue undissolved on boiling will be  $\text{BaSO}_4$  or  $\text{SiO}_2$  or both. Filter this off through the same filter paper on which the residues were collected. Wash with water until a drop of the filtrate gives no yellow precipitate with a solution of potassium chromate.

To the filtrate add 5–10 ml. conc.  $\text{H}_2\text{SO}_4$ , and evaporate down to dense fumes with constant agitation to prevent bumping. Cool. Add 30 ml. water cool. Add 10 ml. of absolute alcohol. Shake well, let stand, filter through a Gooch crucible. Wash first with solution No. 1 and finally with alcohol. Ignite at about 500–600°C. in a muffle. In the absence of a muffle or even in its presence, where only one or two ignitions are to be conducted, the following procedure is adopted :—

Cut a hole in an asbestos board of a diameter sufficient for the introduction of the Gooch crucible. The board with the crucible rests on a second porcelain crucible which latter is heated over a burner. This device avoids contact with reducing gases from the flame which will tend to reduce  $\text{PbSO}_4$  to  $\text{PbS}$ .

NOTES :—

(1) See Expt. 78A-1 for the preparation of the Gooch crucible.

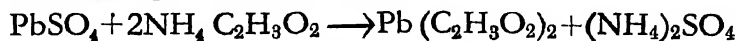
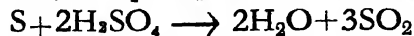
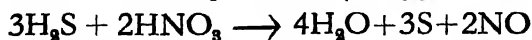
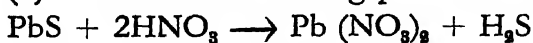
(2) Lead sulphate is less soluble in alcohol than in water. Hence the use of alcohol for final washing. The solubility of lead sulphate in water at 40°C. is 0.0056 gm. The volume of liquid from which lead sulphate is thrown down should be guided by this figure.

(3) Very strong heating decomposes  $\text{PbSO}_4$ . The decomposition begins at 637°C.

(4) The ordinary method of filtering through a filter paper, igniting the sulphate, redissolving any re-

duced sulphide in  $\text{HNO}_3$  followed by sulphuric acid to convert the nitrate into  $\text{PbSO}_4$ , does not yield very accurate results on account of mechanical losses in the process. Moreover, it is lengthy.

(5) The reactions taking place are as follows :—

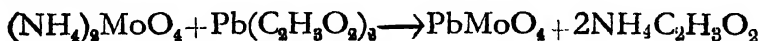


#### EXPERIMENT 62E.

### Determination of Pb in Lead ore by Titration with Ammonium Molybdate Solution

#### Principle :—

When ammonium molybdate solution is added from a burette to a boiling hot solution of lead acetate containing acetic acid, lead molybdate is precipitated. The completion of the precipitation is indicated by adding a drop of the titration mixture to a spotting plate containing a drop of tannin solution. The formation of a brown colour shows that the following reaction is at an end:—



#### Solutions Required :—

1. Standard ammonium molybdate solution :—  
Dissolve 5.7315 gms.  $(\text{NH}_4)_2\text{MoO}_4$  in a litre of water.  
1 ml. of this solution = 0.0005 gm. Pb.
2. Tannin  $\text{C}_{14}\text{H}_{10}\text{O}_9$ . Dissolve 0.5 gm. in 100 ml. water.
3. Dil.  $\text{H}_2\text{SO}_4$ . The same as in Expt. 62D.
4. Ammonium acetate solution. The same as in Expt. 62D.

**Procedure :—**

Proceed exactly as in Expt. 62D until the lead sulphate is purified by treatment with  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  and is changed to lead acetate. Add 5-10 ml. glacial acetic acid. Heat to boiling. Run the molybdate solution from a burette in 2 or 5 ml. portions. Test between additions. When a brown colour appears on the spotting plate, the end-point is reached.

**Standardization of Ammonium Molybdate :—**

As the composition of ammonium molybdate is not very well defined, the solution must be standardized against pure lead foil, or pure lead sulphate. In the former case, proceed as follows :—

Dissolve 0.2000 gm. of the foil in 10 ml. of 1.1 s.g.  $\text{HNO}_3$ . Boil to expel nitrous fumes. Dilute to 50 ml. with water. Add 5 ml. conc.  $\text{H}_2\text{SO}_4$ . Heat to fumes. Cool. Add cautiously 20 ml. of solution No. 3 and 10 ml. ethyl alcohol (90%) Filter. Wash with 100 ml. of the same alcohol. Dissolve the precipitate in conc. ammonium acetate solution. Add 5ml. glacial acetic acid. Heat to boiling. Run the molybdate solution until a drop of the titration mixture gives a brown colour with the indicator on the spotting plate.

**NOTES :—**

It is not advisable to neutralise the excess of  $\text{H}_2\text{SO}_4$  present along with  $\text{PbSO}_4$  by means of ammonia, then dissolve in  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  and acetic acid and follow it up by titration with molybdate. The presence of large quantities of ammonium salts interferes with the accuracy of results.

**EXPERIMENT 63.****Analysis of a sample of Cobalt ore.**

A qualitative examination of the ore revealed the

presence of the following:—As, Fe, Al, Ni, CaO MgO, S, CO<sub>2</sub> and SiO<sub>2</sub>.

**Outline of Procedure :—**The sample is dissolved in nitric acid, evaporated nearly to dryness, redissolved in HCl and filtered. The residue is 'Insoluble Matter'. The filtrate is boiled with sulphurous acid, excess of sulphur di oxide expelled by boiling and the arsenic thrown down as As<sub>2</sub>S<sub>3</sub> by passing H<sub>2</sub>S. The precipitate is filtered off, boiled with water and the resulting solution of arsenious acid titrated against a standard solution of iodine in the presence of a liberal amount of sodium bicarbonate. The filtrate from As<sub>2</sub>S<sub>3</sub> is freed from H<sub>2</sub>S by boiling, the reduced iron oxidised to the ferric state and the separation of iron and aluminium as basic acetates effected as in Expt. 21. Ni and Co are thrown down as sulphides from the filtrate from the basic acetates. The sulphides are filtered off, ignited to oxides and then dissolved in HCl. The solution is made up to a definite volume. From an aliquot part of the solution nickel is determined as in Expt. 28, using the dimethyl glyoxime reagent. From a second aliquot part of the solution, cobalt is determined as in Expt. 30, using the  $\alpha$ -nitroso  $\beta$  naphthol reagent. CaO and MgO are determined from the filtrate from NiS and CoS, as in limestone, Expt. 11. Sulphur is determined by fusion of the sample with Na<sub>2</sub>O<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> in a nickel crucible followed by solution of the cold melt in water, filtration, evaporation of the filtrate with HCl to dryness, re-solution in dil. HCl, filtration to remove silica and precipitation of the H<sub>2</sub>SO<sub>4</sub> by BaCl<sub>2</sub>. The ppt. of BaSO<sub>4</sub> is filtered off, ignited and weighed. From the weight of BaSO<sub>4</sub> sulphur is calculated. Ignition of an exactly weighed quantity of the ore gives the 'Loss on Ignition.'

**Procedure :—**Weigh a 1 gm sample of the ore



( through 100 mesh ) into a 200 ml. capacity beaker. Add 5 ml. of conc.  $\text{HNO}_3$ . Cover with a cover glass, heat over a mush-room top burner until most of the liquid is evaporated off. Cool somewhat, add 25 ml. of water and 5 ml. of conc.  $\text{HCl}$ . Boil for 2 to 3 minutes, filter off the residue on a 7 cm. filter-paper, collecting the filtrate in a 400 ml. beaker. Wash the residue on the paper with 1 : 4  $\text{HCl}$  and then with water until free from  $\text{HCl}$ . Dilute the filtrate to about 100 ml. with water, add 20 ml. of conc.  $\text{HCl}$ , and 1-2 gms. of  $\text{Na}_2\text{SO}_3$ , boil down to about 75 ml., dilute to 200 ml. with water and repeat boiling until the vapours are free from  $\text{SO}_2$ . Test with a strip of filter-paper moistened with  $\text{K}_2\text{Cr}_2\text{O}_7$  solution. Pass a current of  $\text{H}_2\text{S}$  through the solution for 20-30 minutes. Filter, wash the residue with  $\text{H}_2\text{S}$  water and collect the filtrate in a 600 ml. beaker. When the wash liquid is free from  $\text{Fe}$ , transfer paper with the residue to a 750 ml. beaker and add about 600-700 ml. of water. Boil until the volume is reduced to about 300 ml. This operation leads to the hydrolysis of  $\text{As}_2\text{S}_3$ , the product formed being  $\text{As}(\text{OH})_3$ . Cool to room temp., add 5 to 8 gms. of  $\text{NaHCO}_3$  and add 0.1 N-Iodine solution using starch as indicator until a blue colour is obtained.

Boil off  $\text{H}_2\text{S}$  from the filtrate from  $\text{As}_2\text{S}_3$ , add 2 ml. of conc.  $\text{HNO}_3$ , boil; cool, add a solution of  $(\text{NH}_4)_2\text{CO}_3$ , from a dropping bottle until a ppte., which slowly dissolves on stirring, appears. Dilute to 500 ml. with water. Heat to  $90^\circ\text{C}$ ., add 5 ml. of a saturated solution of ammonium acetate, boil for a minute or two and filter. Receive the filtrate in a 1000 ml. beaker. Pass  $\text{H}_2\text{S}$  through the filtrate until precipitation of  $\text{Ni}$  and  $\text{Co}$  is complete. Filter, wash the residue with  $\text{H}_2\text{S}$  water containing 1-2 gms of ammonium acetate per 100 ml. of solution until free from  $\text{Ca}$  and  $\text{Mg}$  salts. Ignite the residue in a porcelain crucible so as to convert the

sulphides, to oxides, cool, dissolve the oxides in 5 ml. of conc. HCl in the crucible, applying gentle heat. Transfer solution to a 100 ml. graduated flask, rinse the crucible 3 or 4 times with water and add the rinsings to the flask. Make up to the mark. Mix well, pipette off 20 ml. of the solution to a 250 ml. beaker, add 100 ml of water, heat to  $50^{\circ}\text{C}$ , add 10 ml. of a 1 % alcoholic solution of the dimethylglyoxime reagent, add 6 N-ammonia solution until alkaline to litmus paper, let stand overnight, filter through a Gooch crucible and finish as in Expt. 28. Pipette off a second aliquot part (20 ml.) to a 400 ml. beaker. Convert the chlorides of Ni and Co into sulphates by heating to fumes with 2-5 ml. of conc.  $\text{H}_2\text{SO}_4$ . Cool. Dissolve the sulphates in 50 ml. of water. Add 1-2 gms. of ammonium persulphate to convert the cobaltous into the cobaltic state. Boil for 5-10 minutes, dilute to 100 ml. with water and add a freshly prepared solution of the  $\alpha$  nitroso  $\beta$  naphthol reagent in excess, add 5 ml. of conc. HCl, heat to about  $50^{\circ}\text{C}$ ., let stand, filter, ignite, cool and weigh (see Expt. 30.) The composition of the ignited residue is not very definite. When quantities of cobalt amounting to more than 5 mgms. are present, dissolve the same in 5 ml. of conc.  $\text{H}_2\text{SO}_4$ , fume, transfer solution to a 100 ml. beaker, add ammonia until strongly ammonical ( 30-40 ml. of 0.96 s. g. ammonia per 100 ml. of solution ) and deposit Co on a platinum cathode using a current density of 0.2 to 0.3 ampere per 100 sq. cms. of cathode surface. The electrolysis will be complete in 1-2 hrs. Get the weight of the cobalt deposit exactly as in the case of the determination of nickel by electrolysis.

Ignite the residues from the basic acetate separation and obtain  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  as in Expt. 56.

Determine the percentages of CaO and MgO from

the filtrate from the sulphides of nickel and cobalt, as in Expt. 11.

Determine sulphur by fusion of 0.2 gm. sample of the ore in a nickel crucible with a mixture of 3 gms of  $\text{Na}_2\text{O}_2$  and 1 gm. of  $\text{Na}_2\text{CO}_3$ , extraction of the cold melt with water, filtration, evaporation of filtrate to dryness with  $\text{HCl}$  followed by re-solution of the evaporated residues in dil.  $\text{HCl}$ , filtration of the silica and determination of S from the filtrate by throwing the sulphuric acid down as  $\text{BaSO}_4$  and finishing in the usual manner.

NOTES :—

1. Evaporation of the ore with  $\text{HCl}$  is not to be adopted as arsenic will be lost. Even boiling of the ore with  $\text{HCl}$  is not permissible as a mixture of  $\text{HCl}$  and  $\text{AsCl}_3$  volatilises completely at about  $107^\circ\text{C}$ ., though the boiling point of pure  $\text{AsCl}_3$  is  $132^\circ\text{C}$ .

2. The usual qualitative method of separation of iron and aluminium as hydroxides by ammonia is not available as appreciable amounts of nickel and cobalt salts are occluded by the hydroxides of iron and aluminium.

3. The dimethylglyoxime reagent should be added in excess. Though this reagent does not precipitate cobalt, it reacts with it forming a soluble compound. Hence enough of it should be present to react with both nickel and cobalt.

4.  $\alpha$ -nitroso  $\beta$  naphthol gradually decomposes on standing. The change is made evident by the reagent which, in the fresh condition, is yellow, assuming a brown or black colour. It may be purified by dissolving 1 gm. of the reagent in 25 ml. of a 4%  $\text{Na}_2\text{CO}_3$  solution, filtering off the portion insoluble, adding to filtrate dil.  $\text{H}_2\text{SO}_4$  (1 : 3) until the medium is acid. The ppt. that appears is the pure reagent. It is filtered off, washed with water and dried between pieces of filter paper.

## EXPERIMENT 64.

**Analysis of Beryl.****Principle:—**

When the finely powdered mineral is sintered with sodium silicofluoride, the fluorides of Be, Al, and Fe, are formed and  $\text{SiO}_2$  is volatilised as  $\text{SiF}_4$ . The sintered mass is extracted with water and filtered. The residue on the filter paper consists of  $\text{AlF}_3$  and  $\text{FeF}_3$  and the filtrate consists of  $\text{BeF}_2$ ,  $\text{Na}_2\text{BeF}_4$  and  $\text{Na}_2\text{SiF}_6$ , small amounts of  $\text{AlF}_3$  contaminating the beryllium fluoride. This is treated in a platinum dish with  $\text{H}_2\text{SO}_4$  when the sulphates of the metals are formed. Be is precipitated as the hydroxide from the sulphate solution by  $\text{NH}_4\text{OH}$ . The ppt. is filtered off, dissolved in nitric acid, and the hydroxide reprecipitated by the addition of  $\text{NH}_4\text{OH}$ . The ppt. is filtered off, washed with water, ignited and weighed.

**Procedure for  $\text{BeO}$  :—**

Mix 1 grm sample of - 120 mesh ore with 1 gm. of sodium silicofluoride on a glazed porcelain tile and introduce the mixture into a porcelain or platinum crucible. Heat in an electric muffle furnace at  $670^\circ$  to  $700^\circ\text{C}$  for one hour. Withdraw the crucible from the furnace, cool, transfer the contents to a 250 ml. beaker, treat with 50 to 75 ml. of water, boil and filter. Collect the filtrate in a platinum dish. Wash the beaker and the residue on the paper with water, ( 4 or 5 times. ) . Add 5 to 10 ml. of 1 : 1  $\text{H}_2\text{SO}_4$  to the contents of the platinum dish and evaporate on the hot plate to fumes of  $\text{SO}_3$ . Extract the residues with water, transfer solution to a 400 ml. beaker, neutralise with  $\text{NH}_4\text{OH}$  and add a small excess of it. Boil for a minute or two. Let the ppt. settle and filter hot. Wash the residue 2 or 3 times by decantation with hot water. Pour 20 ml. of dil.  $\text{HNO}_3$  ( s.g. 1.2 ) on the

filter paper, collecting the solution in the beaker in which the bulk of the ppte. is contained. Add  $\text{NH}_4\text{OH}$  of 0.96 s.g. until the ammonia is in slight excess. Boil and filter. Wash the ppte., ignite it in a platinum crucible at  $950^\circ\text{C}$ ., cool and weigh as  $\text{BeO}$ . Calculate the percentage. See Notes.

**Procedure for  $\text{SiO}_2$  :—**Proceed as described in Expt. 75, for the determination of this constituent in a sample of fireclay.

**Procedure for  $\text{Al}_2\text{O}_3$  :—**Proceed with the filtrate from  $\text{SiO}_2$  as in Expt. 75, by adding  $\text{NH}_4\text{OH}$  until alkaline. Boil, filter, ignite and weigh as  $\text{BeO} + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ . For the separation of  $\text{BeO} + \text{Fe}_2\text{O}_3$  from  $\text{Al}_2\text{O}_3$ , fuse the ignited oxides with 10 times their weight of  $\text{Na}_2\text{CO}_3$ . Extract with water, boil, filter, and wash. The residue on the paper consists of  $\text{BeO} + \text{Fe}_2\text{O}_3$ . Ignite it in a platinum crucible and weigh. Subtract from the weight of  $\text{BeO} + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ . The difference gives the weight of  $\text{Al}_2\text{O}_3$ . A direct method for alumina consists in precipitating it as a complex compound by acidifying the filtrate with dil.  $\text{H}_2\text{SO}_4$  (s.g. 1.2), adding ammonia until a slight turbidity appears, clearing it off with a few drops of the above acid and adding at  $50^\circ\text{C}$  a 5% solution of 8-hydroxyquinoline in a 2*N* acetic acid in excess. Add a 2*N* solution of ammonium acetate until a ppte. appears and add 25 ml. more of the same when the precipitation will be complete. The volume of the 8-hydroxyquinoline reagent of 5% strength required for the precipitation of alumina in 1 grm. sample of beryl will be about 30 to 35 ml. Filter off the ppte. through a sintered glass filter crucible, wash with cold water and dry at  $120^\circ$  to  $140^\circ\text{C}$ . to constancy of weight. Multiply by 0.1110 to get the weight of  $\text{Al}_2\text{O}_3$ . For the formula of the reagent, see Expt. 50,

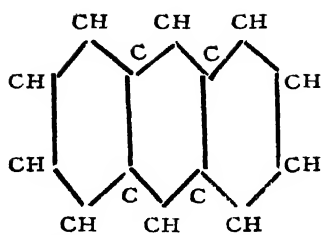
p. 259. The aluminium complex has the formula  $(C_9H_6NO)_3Al$  and contains 5.87% Al.

$Fe_3O_4$  : Subtract the weight of  $BeO$  from the combined weight of  $BeO + Fe_3O_4$

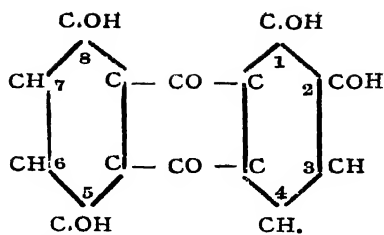
**Qualitative Test for the detection of beryllium in a mineral.** Fuse 0.1 gm. of the mineral powder with 1 to 2 gm. of  $Na_2CO_3$  in a platinum crucible for 5 to 10 minutes ; cool the melt. Extract it with water, and evaporate the solution with excess of  $HCl$  ( 15 to 20 ml. ) in a casserole. Cool. Extract the residues with 10 ml. of dil.  $HCl$  ( 1 : 1 ) . Filter off silica. Add 1 gm  $NH_4Cl$  to the filtrate and then add  $NH_4OH$  ( s.g. 0.96 ) until ammoniacal. Boil. Filter. Dissolve the residue on the paper in 10 ml. dil.  $HCl$  ( 1 : 1 ) . Add to the solution few drops of a 0.05% solution of 1:2:5:8 tetrahydroxyanthraquinone in a 10%  $NaOH$  solution. Make the solution alkaline by adding the 10%  $NaOH$  solution. The appearance of a blue colour more intense than the colour obtained with the reagent and  $NaOH$  solution in like concentration is the indication of the presence of beryllium. If large amounts are present, a blue precipitate will be formed. A similar colour is given by magnesium salts. The interference is overcome by the cautious addition of bromine water when the colour due to the magnesium compound is destroyed.

The reagent is also known as quinalizarin. Its relation to anthracene may be seen from the structural formulae given on the next page.

The following data re the solubilities of the several compounds met with in the course of this experiment will be found useful :



Anthracene.



1:2:5:8 Anthraquinone.

Formula.	17° C.	100° C.	Formula.	Hot water.	Cold water
$\text{Na}_2\text{SiF}_6$ $\text{BeF}_2$	0.652 very soluble	2.45 very soluble	$\text{AlF}_3$ $\text{FeF}_3$	soluble in- soluble	soluble in- soluble
$\text{Na}_2\text{BeF}_4$	1.47.	2.94.			

NOTES:—The purity of the beryllium oxide is tested by the following procedure :—

Fuse the ignited oxide with 3 gms. of  $\text{KHSO}_4$  in a silica or platinum crucible. Cool. Dissolve the resulting sulphates in water. Neutralize with ammonia till just turbid, clear with a slight excess of dil  $\text{H}_2\text{SO}_4$  (s.g. 1.2), add 10 gms. each of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ . Boil. Add a freshly prepared solution containing 0.5 to 1 gm. of tannin in water. If the aluminium complex with tannin does not form, add, dropwise, ammonia of 0.96 s.g. until precipitation starts. Let stand on the hot plate until the ppte. settles. Add filter paper pulp and filter. Ignite in a platinum crucible and weigh as  $\text{Al}_2\text{O}_3$ . Make the necessary correction in the % of  $\text{BeO}$ .

#### EXPERIMENT 65.

##### Analysis of Copper Matte.

The following are determined in routine analysis at a copper works :—Cu, Fe and S.

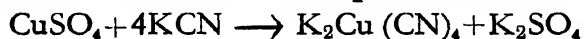
##### Outline of the Process for Cu and Fe :—

The material is brought into solution in conc.

HNO<sub>3</sub> with the help of KClO<sub>3</sub>. The insoluble matter is filtered off. The filtrate is made strongly ammoniacal, the ferric hydroxide filtered off, redissolved in HNO<sub>3</sub> and reprecipitated by ammonia. From the combined filtrates the copper is determined as described in Expt. 59. Alternatively, the cyanide method, described below, may be employed. Fe in the residue on the filter paper is determined as shown in Expt. 10.

**Principle of the Cyanide Method :—**

When a solution of potassium cyanide is added to an ammoniacal solution of a copper salt, a complex cyanide is formed and the blue colour is discharged. The complete discharge of the blue colour marks the end-point. The reaction is represented as follows :—



**Solution required :—**Dissolve 25-30 gms. KCN in 1 litre of water.

**Standardize as follows :—**

Dissolve 0.2-0.3 gm. pure copper in 10 ml. dil. HNO<sub>3</sub> s.g. 1.2. Add ammonia until the precipitated hydroxide is redissolved. Transfer to a 500 ml. conical flask. Dilute to 300 ml. Cool to room temperature and add KCN solution from a burette until the blue colour is discharged. Towards the end, the colour becomes pale violet. If such a solution is allowed to stand for 2-5 minutes, the colour disappears. This should be taken as the end-point. If it does not disappear, more should be added in small quantities and each time 2 minutes allowed for the completion of the reaction.

**Procedure :—**

Dissolve 0.5 gm. sample in a 150 ml. beaker in 10 ml. of conc. HNO<sub>3</sub> saturated in the cold with KClO<sub>3</sub> crystals. Heat very gently on the sand-bath. When no sulphur globules appear after 10 minutes' warming,



increase the heat to boiling. Maintain at a boiling heat for 10 minutes. Transfer solution to a 500 ml. conical flask. Dilute to 200 ml. Add ammonia until a blue solution is obtained. Add 1-2 ml. more. Filter off the  $\text{Fe}(\text{OH})_3$ . Wash twice with water. Redissolve the precipitate in 10 ml. dil.  $\text{HNO}_3$  (s.g. 1.2). Heat to boiling. Reprecipitate Fe by excess of ammonia. Filter off  $\text{Fe}(\text{OH})_3$ . Wash twice. Combine the two filtrates. Dilute to a volume of 300 ml. Titrate with potassium cyanide as in standardization.

### Record and Calculation of results :—

Wt. of pure copper taken	= 0.2000 gm.
Vol. of KCN solution used for this	= 40.0 ml.
Therefore 1 ml. KCN	= 0.005 gm. Cu
Wt. of matte taken	= 0.5000 ml.
Vol. of KCN solution used for matte	= 39.5 ml.
% Cu in matte is	39.5

### NOTES :—

(1) The excess of ammonia, volume of water and temperature must be very nearly the same in the assay as in standardization.

(2) Owing to the fact that  $\text{Fe}(\text{OH})_3$  occludes Cu, it is necessary to adopt a double precipitation for Fe. Some prefer titration without filtering off  $\text{Fe}(\text{OH})_3$ . This procedure saves time and with practice, the exact end point is hit off without difficulty. In fixing the value of the cyanide per ml., it is necessary to add to the pure copper solution iron solution which in quantity amounts to the Fe present in matte.

3. If a lump of sulphur separates when the matte is being brought into solution, it is best transferred to a test-tube and brought into solution by treating with conc.  $\text{HNO}_3$  and bromine. The excess of bromine is

expelled by boiling, the solution added to the main bulk and the determination then proceeded with.

**Iron :—**

Dissolve the ferric hydroxide residue in conc. HCl, reduce with  $\text{SnCl}_2$  and then proceed as in Experiment 10.

**Determination of Sulphur :—**

The sulphur in matte is oxidised to  $\text{H}_2\text{SO}_4$ , by treatment with  $\text{HNO}_3 + \text{KClO}_3$ . The excess of the reagents is removed by repeated evaporation on a water-bath with HCl. The residue is then filtered off.  $\text{BaSO}_4$  is precipitated on adding  $\text{BaCl}_2$  to the filtrate. This is filtered off, ignited and weighed. From the weight of  $\text{BaSO}_4$ , S is calculated.

**Procedure :—**

Weigh a 0.25 gm. sample into a 200 ml. casserole. Add 10 ml. conc.  $\text{HNO}_3$  saturated with  $\text{KClO}_3$ . Cover with a cover-glass. Heat on a water-bath nearly to dryness. Add 5 ml. conc. HCl. Wash down side of the casserole with about 10 ml. water. Evaporate to dryness on a water bath a second time. Repeat evaporation with conc. HCl once again to make sure that all the  $\text{HNO}_3$  is expelled. Take up with 5 ml. dil. HCl (1:1). Dilute with 20 ml. water. Filter. Wash residue. To the filtrate, add ammonia until smelling of ammonia. Boil. Add 10 ml. of 10%  $\text{BaCl}_2$  solution diluted to 50 ml. Redissolve the ferric hydroxide precipitate by the careful addition of dil. HCl. (s.g. 1.1). After it is dissolved, add 2 ml. more of the same HCl. Raise to a boil. Let stand for 1 hour in a corner of the hot plate. Filter. Wash until free from chloride, dry, ignite in a porcelain crucible over a Bunsen burner and weigh. From the weight of  $\text{BaSO}_4$ , calculate the % of sulphur.

**NOTES :—**

1. Heating on the water bath prevents the

volatilisation of  $\text{H}_2\text{SO}_4$  formed by the oxidation of S in matte.

2. Nitric acid, nitrates and chlorates must not be present in a solution from which  $\text{BaSO}_4$  is to be precipitated. Hence their removal by repeated evaporation with HCl is necessary.

3. When  $\text{BaSO}_4$  is precipitated in a solution containing iron, it is contaminated by this metal as shown by the reddish tinge of the ignited precipitate. But when it is precipitated in the manner indicated, it shows no tinge of iron oxide.

### EXPERIMENT 66.

#### Analysis of Iron Blast Furnace Slag.

Determination of  $\text{SiO}_2$ ,  $\text{FeO}$ ,  $\text{MnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{MgO}$ .

The iron blast furnace slag is mostly a mixture of calcium and magnesium silicates with small amounts of  $\text{CaS}$ ,  $\text{MnSiO}_3$ ,  $\text{FeSiO}_3$ , and  $\text{MgO}, \text{Al}_2\text{O}_3$ . This last compound is known as spinel. Slag from a furnace using charcoal as fuel is readily and completely soluble in HCl while that from a furnace using coke as fuel is not so readily and completely soluble in HCl. The method given below is applicable to the latter variety of slag. It is applicable to the former ; only, in this case fusion is unnecessary and therefore omitted.

#### Principle :—

The insoluble silicates of Ca and Mg and the spinel are changed by fusion with  $\text{Na}_2\text{CO}_3$  plus  $\text{K}_2\text{CO}_3$  (fusion mixture) into  $\text{Na}_2\text{SiO}_3$ ,  $\text{NaAlO}_2$  and  $\text{CaO}$  and  $\text{MgO}$ . Solution of the fused mass in HCl yields silicic acid and the chlorides of Al, Ca and Mg.

**Fusion Mixture :—**Mix 10 gms  $\text{Na}_2\text{CO}_3$  with 10gms.  $\text{K}_2\text{CO}_3$ .

**Procedure :—**

Weigh 5 gms. of the above mixture into a platinum crucible. On the top of this introduce 0.5 gm. sample of the finely powdered slag. Mix well with the help of a short glass rod. Brush the rod. Cover with the lid. Heat gently first and then strongly over a Teclu burner maintaining strong heat for about 10-15 minutes. Grip the crucible with a pair of nickel tongs at the end of this time ; take away from the burner and give it a rotary motion so that the melt is distributed all round the side of the crucible. Allow the crucible to cool. When it has cooled sufficiently to be handled, rotate, applying light pressure, between the palms of both hands. By this means, the solidified melt is easily and readily released from the side of the crucible. Place the melt in a 4-5 inch casserole and boil with 20-30 ml. of water. Wash the crucible and lid with hot water and pour the washings into the casserole. Any further residue not removed by water from the crucible is removed by the addition of a few drops of hot dil. HCl and the whole liquid poured into the casserole. When the lumps in it have dissolved, cool to room temperature and add 15-20 ml. of conc. HCl preferably from a burette to avoid frothing over.

**SiO<sub>2</sub> :—**

Cover with a cover glass and evaporate to dryness. Bake for half an hour. The evaporation may be hastened by placing the cover glass on a glass triangle supported on the casserole. The tendency to spit towards the end of the operation is avoided by carrying out the evaporation of the liquid from the surface. This is achieved by supporting the casserole on a broken beaker top. Cut so that it is 6 to 7' in height.

Fig. 21 shows the arrangement. After baking for half an hour, cool. Add 10 ml. conc. HCl and 10 ml. water. Moisten the mass by tipping the basin slightly all round. Boil for 5 minutes. Dilute with 50 ml. hot water. Filter through a 11 cm. paper fitted to a loop funnel. Use hot water for wash. Collect the filtrate in a 400 ml. beaker. Transfer the residue of  $\text{SiO}_2$  from the dish to the filter paper by means of a jet from the wash bottle. A little  $\text{SiO}_2$  adheres to the dish very tenaciously. Remove this by a vigorous application of the

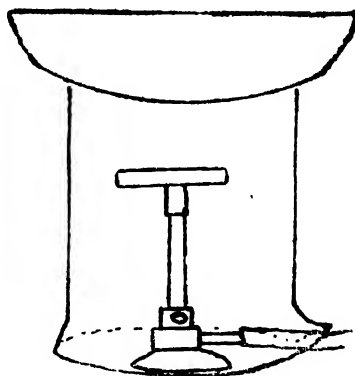
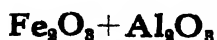


Fig. 21.

'policeman' and transfer to the filter paper. Wash, until free from chloride, with hot water. The beaker with the filtrate is replaced by a second beaker after 4 or 5 washings, the subsequent washings being rejected. The filter paper with the residue of  $\text{SiO}_2$ , contaminated with small amounts of  $\text{TiO}_2$ , is placed in a platinum crucible, dried and gradually ignited until the filter paper is slowly burnt. When the carbon is burnt, maintain the full heat of a Teclu burner for half an hour. Cool the crucible in a desiccator and weigh. Multiply by 200 to get the % of  $\text{SiO}_2$ .

For works' purposes the % of  $\text{SiO}_2$  thus obtained is sufficiently accurate; where great accuracy is required, treatment with  $\text{H}_2\text{SO}_4$  and HF must be adopted. When a mixture of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  is treated with  $\text{H}_2\text{SO}_4$  followed by HF and the same then evaporated to dryness,  $\text{SiO}_2$  is converted into the gas  $\text{SiF}_4$ , Al and Ti remaining as sulphates. By ignition at 800 to 900°C., they are converted into the oxides. If  $\text{H}_2\text{SO}_4$  is not added prior to the addition of HF, all the

three oxides will be changed into fluorides which are volatile. The hydrofluorisation must be carried out in a fume chamber with a good draught. Vapours of HF are poisonous.



From the filtrate precipitate  $\text{Al}(\text{OH})_3 + \text{Fe}(\text{OH})_3$  and finish as in Experiment 12.

### MnO

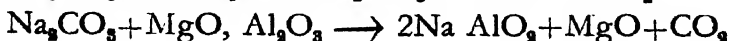
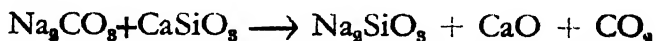
To the filtrate from  $\text{Al}(\text{OH})_3 + \text{Fe}(\text{OH})_3$ , add 1 ml. bromine and then ammonia until ammoniacal. Boil to a faint smell of ammonia. Filter. Ignite residue in a platinum crucible at  $900^\circ\text{C}$ . Cool and weigh. The residue is  $\text{Mn}_2\text{O}_3$  and calculate to MnO.

### CaO and MgO

These are precipitated from the filtrate from MnO  $(\text{OH})_3$  exactly as described under limestone analysis and the determination completed as in Expt. 11.

NOTES :—

(1) The changes taking place on fusion are as follows:—



The solid products to the right of the arrow are soluble in HCl.

(2) Baking is necessary to dehydrate the silicic acid.

(3) Redissolving in HCl is necessary; water will not dissolve any oxychloride of magnesium or oxide of iron that may be formed on baking.

(4) Too high a temperature must not be employed for baking.  $130^\circ\text{C}$ . is about the requisite temperature.

(5) Strong ignition of  $\text{SiO}_2$  is necessary to drive off the water which it holds tenaciously.

(6) In very accurate work, the filtrate from the silica must be evaporated to dryness a second time, the residue redissolved in HCl and then filtered through a second filter paper and the residues from the two filtrations ignited together. This is necessary because of the tendency of small amounts of silicic acid to pass through the filter paper.

(7) On account of the tendency of ignited  $\text{Al}_2\text{O}_3$  to absorb moisture very rapidly, the weighing must be done quickly in a covered crucible.

(8) In the case of slags which are completely soluble in acid, the latter must not be added all at once to the sample. The weighed quantity of slag must be boiled with 15-20 ml. of distilled water and the strong acid added a little at a time, preferably dropwise, to the boiling mixture of slag and water. The addition of the acid all at once to the slag results in the formation of a gelatinous layer of silicic acid which prevents the penetration of the acid and therefore the further attack of the slag.

(9) The solution of the slag is hastened in a few cases by the addition of aqua regia in place of conc. HCl.

(10) A blank for the amounts of  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , CaO and MgO in the reagents used must be run.

### **Sulphur :—**

Proceed by the Evolution method described in Expt. 19. Introduce 2 to 3 gms. of zinc along with 2-3 gms. slag into the evolution flask. The hydrogen evolved helps to carry over  $\text{H}_2\text{S}$  into the absorption vessel.

### **Phosphorus :—**

Weigh 2-5 gms. of the sample in a platinum dish. Dissolve in 20 ml.  $\text{HNO}_3$  of s.g. 1.2. Add 10 ml. HF.

Boil off the latter. Dilute to 100 ml. Filter. Add  $\text{NH}_4\text{OH}$  in excess to the filtrate. Filter. Dissolve the precipitate in  $\text{HNO}_3$  and proceed as in Expt. 16, all the P being present in the precipitate as  $\text{FePO}_4$  or  $\text{AlPO}_4$ . Precipitate as ammonium phospho molybdate and finish by the alkalimetric titration method.

**TiO<sub>2</sub> :—** See Experiment 75.

### EXPERIMENT 67.

#### Analysis of Basic Open-hearth Slag :—

Boil 2.5 gms. of the sample in a 250 ml. beaker with 20 ml. of water. Add 20ml. conc. HCl in small quantities. Evaporate to dryness. Bake for 1 hour at 130° C. Redissolve in 20 ml. dil. HCl (1 : 1) with the aid of heat. Dilute to 50 ml. with water. Filter into a 250 ml. measuring flask. Wash residue with water. Designate the filtrate 'A'. Ignite the filter paper with the residue in a platinum crucible and weigh. Treat with  $\text{H}_2\text{SO}_4$  and HF. Heat, cool and weigh. The difference yields  $\text{SiO}_2$ . Fuse any residue that may be left in the crucible with sodium carbonate (1 gm.), extract with water and dil. HCl. Add extract to the main filtrate 'A'.

#### Principle underlying further Procedure :—

Basic acetate separation is adopted for separating Mn, Ca, Mg from Fe, Al, Ti and  $\text{P}_2\text{O}_5$ . See Expt. 21.

**$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{TiO}_2 + \text{P}_2\text{O}_5$  :—**

Make up the filtrate (A) in the graduated flask to the mark. Mix well. Pipette off 50 ml. into a 400 ml. beaker. Neutralise with ammonia until a precipitate just begins to form. Add drop by drop dil. hydrochloric acid (1 : 1) to clear off any slight precipitate that may have formed. Dilute to 300 ml. with water and heat. When about to boil, add 2-3 ml. of a saturated solution of ammonium acetate. Boil for a minute.

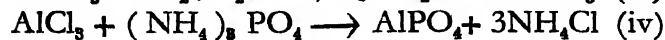
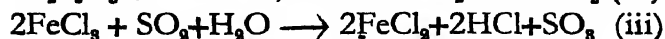
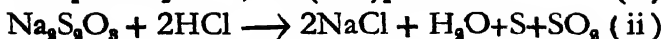


Filter. The residue contains  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{TiO}_2 + \text{P}_2\text{O}_5$ . Ignite and weigh. Use the filtrate for MnO, CaO and MgO determination. From a second 50 ml portion from (A) determine  $\text{Fe}_2\text{O}_3$  as in Expt. 10. From a third portion ( 50 ml. ) determine P as shown in Expt. 16. Determine  $\text{TiO}_2$  by the colour method. See Expt. 75. Use 0.1 gm. sample for the purpose. Fuse with 3 gms.  $\text{KHSO}_4$ .  $\text{Al}_2\text{O}_3$  is obtained by difference

**Procedure for Separation of Ti from Fe, Al and  $\text{P}_2\text{O}_5$  :—**

When a solution slightly acid with hydrochloric acid and containing iron, aluminium, titanium and phosphoric acid is treated with sodium thiosulphate, and acetic acid, the iron is reduced to the ferrous state, remains in solution, the aluminium and the phosphoric acid also remain in solution, while the titanium alone is precipitated as metatitanic acid. This, however, is contaminated by small amounts of iron, aluminium and phosphoric acid. To free the titanic acid from these, fusion with sodium carbonate in a platinum crucible, extraction with water and filtration of the solution are necessary. The residue on the paper is sodium metatitanate. This is dissolved in dil. sulphuric acid and the determination of titanium completed by the Colour method with hydrogen peroxide, Expt. 37 or 75.

The filtrate from the sodium carbonate extraction is added to the filtrate resulting from the first precipitation of titanic acid in an impure form. Aluminium is determined from the combined filtrates by throwing it down as aluminium phosphate. The iron is kept as before in the ferrous state by the addition of sodium thiosulphate. Ammonium phosphate is added to precipitate the aluminium and ammonium acetate is added to react with the free mineral acids resulting from the reactions represented by the following equations :—



The determination of iron can be made from the filtrate from the aluminium phosphate by boiling off the  $\text{SO}_3$ , cooling in a current of  $\text{CO}_2$  and titrating against 0.1N- $\text{KMnO}_4$ . Such a procedure though lengthy has the merit that it is accurate. Determination of iron from an aliquot part of the solution of the slag by the usual method of reduction with zinc without a preliminary separation of the titanium, gives high values for iron.

#### **Procedure for the direct determination of $\text{Al}_2\text{O}_3$ :—**

The basic acetate precipitate is dissolved in  $\text{HCl}$ . This solution is used.

To the cold solution, diluted to 300 ml. concentrated ammonia is added, drop by drop, until a slight permanent precipitate is formed. One and one-half millilitres of concentrated hydrochloric acid are added, and, after the precipitate has dissolved, 50 ml. of a 20 per cent solution of sodium thiosulphate and 10 ml. of acetic acid, in the order named, are added. The solution is boiled ten minutes ; the titanous acid is thus completely precipitated, but is accompanied, however, by a part of the alumina and phosphoric acid and small amounts of iron. After allowing a few minutes for the precipitate to settle, the solution is filtered, the filtrate being received in an 800 ml. beaker, and the precipitate is washed with a hot two per cent solution of acetic acid.

To the filtrate, 30 ml. of a ten per cent solution of ammonium phosphate and one-half millilitre of concentrated hydrochloric acid are added. If a precipitate remains after stirring thoroughly, another portion of

concentrated hydrochloric acid is added, and the solution is stirred until the precipitate dissolves. Thirty ml. of 20% sodium thiosulphate solution are now added. The solution is heated to boiling, 15 ml. of a twenty per cent solution of ammonium acetate are added, and the boiling is continued for ten minutes. The precipitate of aluminium phosphate is allowed to settle, collected on a filter, and washed with hot water. It is dissolved on the paper with very hot hydrochloric acid (1 : 1) the solution being received in the beaker in which the precipitation was effected. This solution is reserved for a second precipitation of alumina after the alumina which is recovered from the preliminary titanous acid precipitate has been added to it. This alumina is recovered as follows :—

The impure titanous acid is ignited in a platinum crucible and the contents fused with sodium carbonate. Of this use a quantity ten times the weight of the ignited precipitate. Extract with water and boil the solution in a 250 ml. beaker for 10 minutes. Let stand and filter through a close-grained paper. Wash precipitate (C) with a one per cent sodium carbonate solution.

Add the filtrate to that obtained from the solution of the aluminium phosphate in dil. HCl. Repeat the precipitation of aluminium phosphate from this solution. Add 30 ml. of 10% ammonium phosphate solution. Clear off any precipitate that separates out by the dropwise addition of dil. HCl. Add 30 ml. of a 20 % solution of sodium thiosulphate. Heat to boiling, add 15 ml. of a 20 % solution of ammonium acetate. Continue boiling for 10 minutes. Let stand, filter, ignite in a porcelain crucible and weigh as  $\text{AlPO}_4$ .

**TiO<sub>2</sub> :—**

Dissolve precipitate (C) by pouring hot dil.  $\text{H}_2\text{SO}_4$  (1 : 3) on it. Wash the filter paper 2-3 times with the

same acid. Determine either by the colour method of Expt. 37 or 75 or by precipitation of  $\text{Ti}(\text{OH})_4$  by hydrolysis of the titanium sulphate, providing excess of thiosulphate and acetic acid.

### **MnO:—**

To the filtrate from  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{TiO}_2 + \text{P}_2\text{O}_5$ , add 2-3 ml. of liquid bromine. Add 20 ml. ammonia (s.g. 0.88). Boil until faintly smelling of ammonia. Filter. Wash. Ignite residue in a platinum crucible at  $900^\circ\text{C}$ . From the weight of  $\text{Mn}_3\text{O}_4$ , calculate MnO.

**CaO and MgO:—** For these proceed with the filtrate from MnO determination, exactly as shown in Expt. 75.

## **EXPERIMENT 68.**

### **Acid Open Hearth Slag.**

Unlike basic open hearth slag, this is opened out by a fusion attack followed by treatment with HCl. This is the only point of difference in the analytical procedure. The constituents determined are the same as in the basic open hearth slag.

### **Procedure:—**

Fuse 0.5 gm. sample in a platinum crucible with 5 gms.  $\text{Na}_2\text{CO}_3$  or fusion mixture. Proceed after fusion as in the case of iron blast furnace slag (Experiment 66).

## **EXPERIMENT 69.**

### **% Calcium Carbide in Electric Furnace Slag.**

### **Principle:—**

The sample of slag is weighed and introduced into a previously weighed Schrotter's apparatus. Water is introduced in the reservoir compartment. The whole apparatus is then weighed. The water is allowed to

act on the carbide. The gas ( acetylene ) generated, in the vessel passes out of the flask, being deprived of its moisture content by means of the anhydrous  $\text{CaCl}_2$ , contained in the fused-on attachment to the apparatus. After complete expulsion, the apparatus is weighed. The loss in weight represents the weight of acetylene gas. From this weight, the amount of carbide of calcium is calculated and hence its percentage in the slag.

The reaction taking place is as follows :—



Procedure :—The apparatus used is shown in Fig. 19b. Clean and dry the apparatus. Introduce sifted anhydrous  $\text{CaCl}_2$  into A. Weigh the apparatus. Introduce 5-10 gms. of the finely powdered slag into the flask. Weigh. Difference gives the weight of slag taken. Introduce about 5-10 ml. of water into F, keeping the tap c closed. Weigh the whole apparatus. Open c and allow the water to act on the slag for 30 minutes at room temperature and then gently heat the apparatus so that the contents just boil. Aspirate a current of dry air through the apparatus at the rate of 2-3 bubbles per second. The gas leaves the apparatus after its moisture is absorbed by the anhydrous  $\text{CaCl}_2$ . Cool. Wipe the outside of the apparatus with chamois leather piece and then weigh. The loss of weight represents the weight of acetylene. From this, the weight of  $\text{CaC}_2$  in the quantity of slag taken is calculated. 26 gms. of acetylene correspond to 64 gms. of calcium carbide.

NOTES :—

(1) The clean flask is dried by adding about 5 ml. of rectified spirit, wetting it all over, pouring out the excess and passing a current of hot air through a glass delivery tube reaching to the bottom of the flask. Allow to cool in air. Wipe the outside with a piece of

chamois leather before weighing. In this way any moisture on the outside is eliminated. This same operation of wiping is conducted each time the flask is weighed.

(2) Acetylene is somewhat soluble in water. By boiling, the gas is expelled.

(3) At the start the apparatus is weighed when filled with air. At the end of the experiment, it should be weighed, also filled with air. Hence the stream of dry air entering at d and drawn out at e. The stream of air should be dry. Hence the necessity for passing the entering stream through anhydrous  $\text{CaCl}_2$  tube, attached to d temporarily.

(4) The ends d and e should be plugged up with glass rods inserted into pieces of rubber tubing to prevent entry of moisture during weighing.

(5) Methods involving the absorption of  $\text{C}_2\text{H}_2$  by suitable reagents, the liberation thereof by subsequent treatment with other reagents and the volumetric titration of the same in a manner similar to that employed for S determination in pig iron and steel have not yet been evolved.

(6) A qualitative test for the detection of acetylene gas present in a gaseous mixture consists in the formation of a red coloured ppte. when the gas is led through a few drops of the following solution diluted to 500 ml. :—

Weigh 1 gm. copper nitrate into a 50 ml. measuring flask. Dissolve in 5 ml. of water. Add 4 ml. of 6 N ammonia and 3 gms. of hydroxylamine hydrochloride and shake until the solution is colourless. Place a few drops of this mixture into a stoppered 500 ml. cylinder. Dilute with water and mix. Bubble the gas mixture through this solution until the solution becomes pink.

Shake. A beautiful red coloured ppte. of copper acetylide indicates the presence of acetylene in the mixture of gases.

(7) Alternatively the content of calcium carbide in slags may be calculated on the basis of two determinations.

Combustion of a known quantity of the slag in a stream of oxygen using the apparatus for the determination of carbon in steel by combustion (p. 129) yields the total carbon. The amount of free carbon is ascertained on a known weight of a second sample by treating it with dil. HCl, filtering off the undissolved matter through asbestos, drying this and carrying out the combustion of the dry residues. Subtraction of the % of carbon as ascertained by the second run from that obtained from the first run yields carbon which is calculated to calcium carbide.

### EXPERIMENT 70.

#### Determination of Cu in Dump Slag.

The amount present is about 0.2%. A colorimetric method is the one generally adopted. The blue colour produced by solution of the sample in  $\text{HNO}_3$  followed by treatment with ammonia is compared with that produced by a standard solution also treated with ammonia.

#### Solution required :—

Dissolve 0.1 gm. copper contained in a 100 ml. beaker in 5 ml. dil.  $\text{HNO}_3$  of s.g. 1.2. Expel nitrous fumes by boiling. Cool. Dilute with water. Add ammonia (s.g. 0.96) until the precipitated hydroxide completely dissolves. Transfer solution to a 100 ml. measuring flask. Make up to the mark with water. Mix thoroughly by shaking.

1 ml. of the solution = 0.001 gm. Cu.

### Procedure for Slag from matte-smelting reverberatory furnace :—

Dissolve 1 gm. of the finely powdered material in 10 ml. conc.  $\text{HNO}_3$  and a few crystals of  $\text{KClO}_3$ . Heat till the brown fumes are expelled. Dilute with water. Heat until dissolved. Cool. Add  $\text{NH}_4\text{OH}$  in excess. Filter off  $\text{SiO}_2$ ,  $\text{Fe}(\text{OH})_3$ , etc., receiving the filtrate in a 100 ml. graduated tube. Bring to the mark. Introduce a mixture of water and dil. ammonia into a second graduated tube up to the 100 ml. mark. Add the standard solution from a burette in small quantities. Mix and compare the sample, after adding an equal volume of water, with the standard until the tints are equal. 2.2 ml. of the above standard Cu solution matched the colour of the sample. Hence % Cu in the slag is 0.22.

### EXPERIMENT 71.

#### Slag from a Bessemer Converter Producing Blister Copper.

Reduce the slag to a fine powder in an agate mortar. Weigh out 2 gms. into a platinum dish, add 10 ml. HF. Allow to stand for 1 hour, stirring occasionally with platinum wire. Add 2 ml. conc.  $\text{H}_2\text{SO}_4$ , evaporate to a syrup on a water bath and finally volatilise the  $\text{SiO}_2$  by stronger heating.

#### Procedure for Copper :—

Take up with  $\text{HCl}$  and  $\text{H}_2\text{O}$ , transfer to a beaker, warm, pass  $\text{H}_2\text{S}$ , filter off  $\text{CuS}$  and  $\text{As}_2\text{S}_3$ , wash, dissolve in  $\text{HNO}_3$  +  $\text{KClO}_3$ , add a drop of  $\text{FeCl}_3$  (equivalent to about 0.05 gm Fe) and then excess  $\text{NH}_4\text{OH}$ , filter, wash, evaporate filtrate to small bulk, and determine copper colorimetrically as in Experiment 70 or electrolytically as in Experiment 43.



**NOTE :—**

Addition of  $\text{FeCl}_3$  has for its object the separation of arsenic as ferric arsenate. This separates out along with ferric hydroxide on the addition of  $\text{NH}_4\text{OH}$ .

**Arsenic :—**

Redissolve in  $\text{HCl}$  the precipitate formed by the addition of  $\text{FeCl}_3$  followed by  $\text{NH}_4\text{OH}$  and precipitate As as  $\text{As}_2\text{S}_3$  by passing  $\text{H}_2\text{S}$ , filter, wash, dissolve the ppt. in  $\text{HNO}_3$  and  $\text{KClO}_3$ , dilute, add magnesia mixture, allow to stand for several hours, filter, wash, ignite in a porcelain crucible and weigh as magnesium pyroarsenate having the formula  $\text{Mg}_3\text{As}_2\text{O}_7$ . The precipitate separating out on the addition of magnesia mixture is magnesium ammonium arsenate.

**NOTE :—**

The conditions of precipitation and ignition of  $\text{MgNH}_4\text{AsO}_4$  are exactly similar to those of  $\text{MgNH}_4\text{PO}_4$  which are described in Expt. 11.

**Ferric oxide and Alumina :—**

To the filtrate from the first precipitation of Cu and As as sulphides, add a drop of  $\text{HNO}_3$ , boil off  $\text{H}_2\text{S}$ , add  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$ , boil and filter off  $\text{Fe}(\text{OH})_3 + \text{Al}(\text{OH})_3$ , dry, ignite and weigh as oxides.

Digest the ignited oxides at the ordinary temperature for 1 hour with conc.  $\text{HCl}$ , heat until dissolved, reduce with  $\text{SnCl}_2$  and determine Fe as in Expt. 10. Obtain  $\text{Al}_2\text{O}_3$  by difference.

**Lime :—**

To the filtrate from  $\text{Fe}(\text{OH})_3 + \text{Al}(\text{OH})_3$ , add  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , filter and proceed as in Experiment 11.

**Magnesia :—**

Evaporate filtrate to half bulk, add  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{HPO}_4$ , stir well, allow to stand for several hours, filter, wash, ignite and weigh as  $\text{Mg}_3\text{P}_2\text{O}_7$ .

**Alkalies :—**

Evaporate filtrate from above to dryness, destroy ammonium salts, moisten with 3 to 5 drops of dil. HCl. (1 : 1). Heat to dull redness. Cool and weigh. The weight represents KCl+NaCl. For the determination of  $K_2O$  and  $Na_2O$  separately, see Expt. 77.

**Silica :—**

Fuse 1 gm. with 6 gms. 'fusion mixture' in a platinum dish, extract melt with water, filter, acidify filtrate with HCl, evaporate to dryness, take up with HCl, filter, dry, ignite and weigh as impure  $SiO_2$ . Volatilise with  $H_2SO_4$  and HF as usual. Loss represents  $SiO_2$ . See Experiment 66 for details.

**EXPERIMENT 72.****Analysis of Copper Refinery Slag.**

The method described in Experiment 71 may be adopted without any modification.

**Procedure for  $iO_2$  :—**

Dissolve 1 gm. of the finely ground material in a 250 ml. beaker with 20 ml. conc.  $HNO_3$  and a few crystals of  $KClO_3$ . Evaporate to dryness. Take up with 20 ml. dil. HCl (s.g. 1.1), filter. Wash. Ignite the residue and weigh as  $SiO_2$ .

**Copper :—**

Pass  $H_2S$  into the filtrate. Filter off  $CuS$ , dissolve the precipitate in 10 ml. boiling hot dil.  $HNO_3$  s.g. 1.2, and filter off any insoluble sulphide of As. From the filtrate determine Cu by the cyanide method. See Experiment 59.

**Iron :—**

Boil the filtrate from  $CuS$  to expel  $H_2S$ , oxidise with a drop or two of  $HNO_3$ . Cool, add  $NH_4OH$ . Boil. Filter off the precipitate, dissolve in HCl, reduce with  $SnCl_2$ , and proceed as in Experiment 9 or 10.

**Nickel :—**

To the filtrate from the ferric hydroxide precipitate, add ammonium sulphide until nickel is completely precipitated as  $\text{NiS}$ . Filter. Wash. Ignite in a porcelain crucible to oxide. Dissolve in  $\text{HCl}$ . Precipitate nickel as nickel dimethyl glyoxime and finish as in Expt. 28.

To the filtrate from  $\text{NiS}$ , add  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  and filter off  $\text{CaC}_2\text{O}_4$ . Determine  $\text{CaO}$  as in Experiment 11.

**EXPERIMENT 73.****Analysis of Slag from a Lead Blast Furnace.****Determination of Lead.****Principle :—**

The slag is readily opened out with a mixture of  $\text{HCl}$  and  $\text{HNO}_3$ .  $\text{H}_2\text{SO}_4$  precipitates lead as  $\text{PbSO}_4$ . This is filtered off along with  $\text{BaSO}_4$  and  $\text{SiO}_2$ . Separation of  $\text{PbSO}_4$  from  $\text{BaSO}_4$  and  $\text{SiO}_2$  is effected by ammonium acetate

**Procedure :—**

Dissolve 2-5 gms. of the slag in 15 ml. conc.  $\text{HCl}$ , add a few ml. of conc.  $\text{HNO}_3$ , evaporate to dryness, take up with 10 ml. conc.  $\text{HCl}$  and 50 ml.  $\text{H}_2\text{O}$ , add 5 ml. conc.  $\text{H}_2\text{SO}_4$ , and evaporate to fumes. Cool, dilute to 100 ml. with  $\text{H}_2\text{O}$ , boil, let settle, filter, wash with cold 10%  $\text{H}_2\text{SO}_4$ , reserve filtrate (F) for determination of  $\text{Cu}$  (see below). Transfer precipitate from the paper to a beaker with hot water, add 5 gms.  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ , boil, refilter, wash with 2%  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  solution and determine  $\text{Pb}$  from the filtrate by the molybdate method described in Experiment 62.

**Silica :—**

Dry the residue on the filter paper consisting of  $\text{BaSO}_4 + \text{SiO}_2$ . Ignite and weigh. Treat with  $\text{H}_2\text{SO}_4$  and  $\text{HF}$ . Ignite and weigh. The loss in weight represents  $\text{SiO}_2$ .

**Barium :—**

Fuse residue from HF treatment with 5-6 gms. of 'fusion mixture' in a *nickel crucible*, extract with hot water containing a little  $\text{NH}_4\text{OH}$ , filter, wash with very dilute  $\text{NH}_4\text{OH}$  until free from sulphates. Dissolve precipitate off the filter with dil.  $\text{HCl}$ , refilter through the same paper, and add excess of  $\text{K}_2\text{CrO}_4$ , make slightly ammoniacal, boil, settle. Filter, wash with 1 % ammonium acetate solution until free from chromate, dry, ignite at a *moderate temperature* and weigh as  $\text{BaCrO}_4$ .

**Copper :—**

To the original filtrate ( F ) add 5 ml.  $\text{HCl}$ , and pass  $\text{H}_2\text{S}$ , filter off any precipitate of  $\text{CuS}$ , wash, redissolve in a little  $\text{HNO}_3$  and determine Cu by the Iodide method. See Experiment 59.

 **$\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$  :—**

Boil filtrate free from  $\text{H}_2\text{S}$ , oxidise with  $\text{HNO}_3$ , add 2 gms.  $\text{NH}_4\text{Cl}$ , then  $\text{NH}_4\text{OH}$  to a faint smell, boil, filter, wash well, redissolve and reprecipitate, wash, ignite and weigh as combined oxides. Redissolve ignited residue in  $\text{HCl}$  and determine Fe as in Experiment 10. Calculate  $\text{Al}_2\text{O}_3$  by difference. If  $\text{Cr}_2\text{O}_3$  is suspected, determine it as follows :—

Divide the solution of the ignited oxides in  $\text{HCl}$  into two parts. From one part determine iron as described above and from the other determine chromium as follows : Evaporate to fumes with  $\text{H}_2\text{SO}_4$ , dilute with water, boil, add a 2% solution of  $\text{KMnO}_4$  until a pink colour persists on boiling for some minutes. Redissolve any separated residue of  $\text{MnO}_2$  in conc.  $\text{HCl}$ . ( Sufficient  $\text{HCl}$  to clear the liquid should be added). Dilute with 150 ml. water. Boil until the smell of chlorine disappears completely. Cool. Add excess of standard  $\text{FeSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $6\text{H}_2\text{O}$ . Titrate excess by standard

$K_2Cr_2O_7$ . 1 ml. 0.1 N- $FeSO_4$ =0.00173 gm. Cr. For the principle of the method, see Expt. 31.

#### **Zinc Oxide :—**

To the filtrate from  $Fe(OH)_3 + Al(OH)_3$ , add  $(NH_4)_2S$ , filter, wash, redissolve in HCl and determine zinc as pyro phosphate. See Experiment 41.

#### **Lime :—**

Boil down filtrate to small bulk and determine after precipitating as  $CaC_2O_4$ . See Experiment 11.

#### **Magnesia :—**

To the filtrate from  $CaC_2O_4$  add aqua regia and boil down to low bulk, add  $H_2O$ , make just alkaline with  $NH_4OH$  and add  $Na_2HPO_4$ , agitate, let stand 6-12 hours, filter, wash, ignite and weigh as  $Mg_2P_2O_7$ .

#### **Sulphur :—**

Dissolve 2 gms. of the slag in aqua regia, evaporate to low bulk, add more HCl and re-evaporate, filter. add  $BaCl_2$ , and determine S as  $BaSO_4$ .

The insoluble residue also contains S. To determine the sulphur in this, fuse with 'fusion mixture' with a little  $KNO_3$ , extract the melt with water, filter off the insoluble matter, acidify the filtrate with HCl, add  $BaCl_2$ , and determine S as  $BaSO_4$ . See Experiment 18.

#### **Gold and Silver :—**

Proceed using the charge shown for a silicious ore described in Experiment 53.

### **EXPERIMENT 74.**

#### **Analysis of Fluorspar.**

#### **General :—**

This is used as a flux in steel making. It is also used in aluminium making. In the latter process, whenever difficulty is experienced in effecting a sharp separation

of the metal from the molten cryolite, it has been used with very great advantage.

The mineral  $\text{CaF}_2$  occurs in association with  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{FeCO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaSiO}_3$ , etc. . It is not completely converted into sodium or potassium fluoride by fusion with  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$ . Its complete attack by fusion is possible only in the presence of a considerable amount of quartz sand or pure silica along with a mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ .

**Principle :—**

The mineral powder is treated with acetic acid.  $\text{CaF}_2$  is only very slightly attacked but  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{FeCO}_3$ , and  $\text{CaSiO}_3$  are dissolved. Dilution with water and boiling followed by filtration yield a residue consisting of  $\text{CaF}_2$ , basic ferric acetate and silica. The filtrate contains  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  and  $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$ . The residue is ignited and weighed. Treatment of the ignited residue with  $\text{HF}$  volatilises the silica. The residue is ignited and weighed. The difference yields the silica content of the mineral. The residue left after  $\text{HF}$  treatment is evaporated to dryness with conc.  $\text{H}_2\text{SO}_4$ . This expels the  $\text{HF}$  leaving behind  $\text{CaSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{H}_3\text{PO}_4$ . The mass is heated strongly and then fused with  $\text{Na}_2\text{CO}_3$ . The fusion is extracted with water, acidified with  $\text{HNO}_3$  and made up to a definite volume in a graduated flask. An aliquot part is used for the determination of  $\text{H}_3\text{PO}_4$  by precipitating with  $(\text{NH}_4)_2\text{MoO}_4$  and finishing as in Expt. 16.

On a second aliquot portion the basic ferric acetate separation of phosphoric acid described in Expt. 21 is adopted. The filtrate from the basic ferric acetate and the ferric and the aluminium phosphate is used for the determination of calcium and magnesium present as  $\text{CaF}_2$  and  $\text{MgF}_2$ . Ca is thrown down as  $\text{CaC}_2\text{O}_4$  and Mg as  $\text{Mg NH}_4\text{PO}_4$ . See Expt. 11.

The residue from the basic acetate separation is ignited and weighed. This yields the sum of  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$ . This is fused with  $\text{Na}_2\text{CO}_3$ , the fusion product acidified with  $\text{H}_2\text{SO}_4$ , tartaric acid added, the solution neutralised with  $\text{NH}_4\text{OH}$  and then made acid with  $\text{H}_2\text{SO}_4$ .  $\text{H}_2\text{S}$  reduces the iron and on making ammoniacal again, iron is precipitated as  $\text{FeS}$ . This is filtered off, ignited and weighed. From the weight of  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$ , subtract the sum of  $\text{Fe}_2\text{O}_3 + \text{P}_2\text{O}_5$ . The difference yields the weight of  $\text{Al}_2\text{O}_3$ .

The filtrate from the solution of the mineral in acetic acid is used for the determination of the amounts of Ca and Mg present as carbonates. They are thrown down as  $\text{CaC}_2\text{O}_4$  and  $\text{Mg NH}_4\text{PO}_4$ . See Expt. 11.

The following represents the scheme of analysis of fluorspar :—

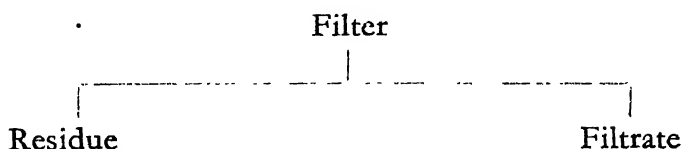
Open out 0.5 gm. sample of the mineral powder with acetic acid.

Dilute with water, boil and filter.

Residue	Filtrate
Ignite and weigh. Treat with $\text{HF}$ , ignite and weigh. Difference is $\text{SiO}_2$ .	Proceed for Ca
Treat with conc. $\text{H}_2\text{SO}_4$ . Heat to drive off $\text{HF}$ . Repeat treatment with $\text{H}_2\text{SO}_4$ and heat to decompose sulphates. Fuse with $\text{Na}_2\text{CO}_3$ . Extract with water and dil. $\text{HNO}_3$ and make up to the 250. ml. mark in a graduated flask. Pipette off three separate portions a, b and c. Portion (a) is 25 ml. and is transferred to a 250-300 ml. capacity conical flask. Precipitate P as $(\text{NH}_4)_3\text{PO}_4$ , 12 MoO <sub>3</sub> , and finish as in. Expt. 16.	as $\text{CaCO}_3$ as shown in Expt.12.

Transfer 100 ml., portion (b), into a 600 ml. capacity beaker and throw down Fe as FeS by the method of Gooch, ignite and weigh as  $\text{Fe}_2\text{O}_3$ . See page 314, Expt. 57. Discard the filtrate from FeS.

Transfer 100 ml. of the solution in the 250 ml. flask, portion (c), into a 600 ml. capacity beaker. Throw down Fe, Al,  $\text{H}_3\text{PO}_4$  as basic acetates and phosphates as described in Expt. 21.



Ignite, cool and weigh as  $\text{Fe}_2\text{O}_3$  + Determine Ca and  $\text{Al}_2\text{O}_3$  +  $\text{P}_2\text{O}_5$ . Subtract from this Mg as in Expt. 11 the sum of  $\text{P}_2\text{O}_5$  as ascertained in This gives the Ca portion (a) and  $\text{Fe}_2\text{O}_3$  as ascertained  $\text{F}_2$  and Mg  $\text{F}_2$  present in portion (c). The difference is sent in the mineral.  $\text{AlPO}_4$ .

### Procedure :—

$\text{SiO}_2$  :—Weigh 0.5000 gm of the sample powdered finely enough to pass through a 100 mesh sieve, into a 200 ml. beaker. Add 10 ml. of 1.5 N—acetic acid. Cover with a cover glass and heat on a water-bath for one hour. Rinse down the lower side of the cover-glass, remove it, evaporate to dryness on the water-bath and bake for 30 minutes. Add 50 ml. of water and boil. Filter, collecting the filtrate in a 400 ml. beaker. Wash residue on the paper with hot water 4 or 5 times, collecting the washing in the same beaker. Transfer filter-paper with the residue to a platinum crucible. Ignite, cool and weigh. Add 5 ml. of HF. and heat on the electric hot plate or a sand-bath until dry.



Repeat treatment with HF once more using 2 ml. Heat as before until dry. Moisten with HF. Add  $\text{NH}_4\text{OH}$  to precipitate Fe. Evaporate slowly to dryness. Ignite strongly. Cool and weigh. Difference gives the weight of silica. Calculate the percentage.

$\text{P}_2\text{O}_5$ :—Add 2-3 ml. of conc.  $\text{H}_2\text{SO}_4$  to the residue in the crucible. Heat on a hot plate until the HF is expelled. This will take 5-10 minutes. Repeat treatment with  $\text{H}_2\text{SO}_4$  and heat to fumes. Prevent loss from liquid creeping to the top of the crucible and the outside by directing the flame of a Bunsen burner held in the hand, to the top of the crucible. When fumes have ceased to be evolved, heat strongly over a Teclu burner. Add 2-3 gms. of  $\text{Na}_2\text{CO}_3$  to the crucible, heat over a Teclu burner until well fused. Cool, extract with water and dil.  $\text{HNO}_3$  (s.g. 1.2) and transfer solution to a 250 ml. measuring flask. Rinse the crucible with water 3 or 4 times and transfer the rinsings to the flask. Make up to the mark with water. Mix thoroughly. Pipette off 25 ml. to a conical flask. Add 15 ml. conc.  $\text{HNO}_3$ . Heat to about  $70^\circ\text{C}$ . and add 60-75 ml. of  $(\text{NH}_4)_2\text{MoO}_4$  solution. Let stand, filter and wash with 1%  $\text{NH}_4\text{NO}_3$  solution until free from acid. Transfer paper with the precipitate to the flask in which the precipitation was made, add excess of 0.2N-NaOH solution from a burette and shake until the yellow ppte. is completely dissolved. Add 0.2N- $\text{HNO}_3$  until excess of NaOH solution is neutralised. Phenolphthalein is the indicator. Calculate to  $\text{P}_2\text{O}_5$ .

$\text{Fe}_2\text{O}_3$ :—Pipette off 100 ml. portion of the solution in the 250 ml. measuring flask to a 400 ml. beaker. Add 10 ml. of 1:1  $\text{H}_2\text{SO}_4$ . Heat to fuming. Dilute with water to 100 ml. Add 1-2 gms. of tartaric acid. Neutralise with  $\text{NH}_4\text{OH}$ .

Make slightly acid with 2-3 ml. of 2 N— $\text{H}_2\text{SO}_4$ . Pass  $\text{H}_2\text{S}$  for 10 minutes. Make ammoniacal and continue to pass  $\text{H}_2\text{S}$  for another 10 minutes. Filter off  $\text{FeS}$ , wash with  $\text{H}_2\text{S}$ -water, ignite in a porcelain crucible, cool and weigh as  $\text{Fe}_2\text{O}_3$ . Discard the filtrate from the  $\text{FeS}$  precipitate. Subtract sum of  $\text{Fe}_2\text{O}_3 + \text{P}_2\text{O}_5$  from the weight of  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$  to be obtained by the procedure given below and calculate the percentage of  $\text{Al}_2\text{O}_3$ .

$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$  :—Pipette off 100 ml. of the filtrate in the measuring flask into a 400 ml. beaker. Neutralise the free acid with a saturated solution of  $(\text{NH}_4)_2\text{CO}_3$ , until a precipitate, dissolving with difficulty on stirring, appears. Dilute to 300 ml. with water. Add 5 ml. of a saturated ammonium acetate solution. Boil and filter. Wash precipitate with hot water, until free from Ca, Mg and Na salts. Transfer ppte. to a porcelain crucible, dry, ignite, cool and weigh as  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$ .

Ca as  $\text{Ca F}_2$  :—Add 40 ml. of a saturated solution of ammonium oxalate in the boiling hot condition to the filtrate from  $\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ . Let stand for an hour. Filter through a close paper, wash with hot water until the washing is free from ammonium oxalate. Transfer ppte. to the beaker in which the precipitation was made by puncturing a hole in the filter-paper and running first hot water, then 10 ml. of 1.2 s.g. hot dil.  $\text{H}_2\text{SO}_4$  and finally hot water. Heat to  $70^\circ\text{C}$ . Add 0.1 N— $\text{KMnO}_4$  until pink. Calculate %  $\text{CaF}_2$ .

Mg as  $\text{Mg F}_2$  :—Add to the filtrate from the above 10 ml. of  $(\text{NH}_4)_2\text{HPO}_4$  (Bench Reagent) and 100 ml. of  $\text{NH}_4\text{OH}$  of s.g. 0.96. Let stand 12 hours, filter, wash with dil. ammonia (1:9), transfer to a porcelain crucible, dry, ignite slowly at first and then strongly. Cool and weigh. From the weight of  $\text{Mg}_2\text{P}_2\text{O}_7$ , calculate %  $\text{MgF}_2$ .

Determination of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  in the filtrate from the solution of the mineral in acetic acid :— Proceed as above or as shown in Expt. 12.

$\text{CO}_2$  :— Heat one gram sample in the combustion furnace used for the determination of carbon in steel. Pass a current of oxygen to sweep out the  $\text{CO}_2$  into the gas collecting burette. Measure the volume of  $\text{CO}_2 + \text{O}_2$ . Pass the mixture through caustic potash solution in the absorption tube. Pass the residual gas back into the burette and measure the residual volume. Difference gives the volume of  $\text{CO}_2$ . Calculate the  $\text{CO}_2$  by weight from the volume of  $\text{CO}_2$  obtained, after reducing the volume to N. T. P. ( normal temperature and pressure ).

NOTES :—

(1) The method described is applicable both to samples of fluor spar and to the phosphatic nodules of Trichinopoly containing cubical crystals of fluor spar.

(2) A direct method of determination of  $\text{CaF}_2$  in a sample is based on throwing down  $\text{Ca}$  as  $\text{CaF}_2$  in admixture with  $\text{CaCO}_3$ . The formation of  $\text{CaF}_2$  along with  $\text{CaCO}_3$  helps filtration. The mixed ppte. is ignited, treated with acetic acid and filtered. The residue is ignited and weighed as  $\text{CaF}_2$ . The purity of the  $\text{CaF}_2$  is tested by evaporating to fumes twice with conc.  $\text{H}_2\text{SO}_4$  and igniting and weighing as  $\text{CaSO}_4$ . The details of procedure are:— Fuse 0.5000 gm. sample in a large size platinum crucible with 1.25 gms. of  $\text{SiO}_2$  and 3 gms of a mixture of equal parts of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  until the evolution of gas bubbles (  $\text{CO}_2$  ) ceases. The temp. of fusion should not exceed  $900^\circ\text{C}$ ., as there is the danger of volatilization of the alkali fluorides. ( M. Pt. of  $\text{NaF}$  is  $980^\circ$  and that of  $\text{KF}$  is  $880^\circ\text{C}$ . ) Cool. Extract with 50-75 ml. of cold water. Boil and filter. Wash residue on the paper with

hot water. Collect the filtrate and the rinsings in a 400 ml. beaker. Nearly neutralize a large part of the  $\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$  with normal  $\text{HNO}_3$ . A blank fusion may be run using the above weights of  $\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3 + \text{SiO}_2$ , extracting with water and adding normal  $\text{HNO}_3$  from a burette using methyl orange as indicator. To the assay add 0.2–0.3 ml. less of the acid than that required by the blank. Add 4 gms. of  $(\text{NH}_4)_2\text{CO}_3$ , heat to  $40^\circ\text{C}$ . and let stand for 12 hrs. Filter off the  $\text{SiO}_2$ . Wash the ppt. with 2%  $(\text{NH}_4)_2\text{CO}_3$  soln. Collect the filtrate and the washings in a casserole and evaporate to dryness on the water-bath. Repeat evaporation with 2 normal  $\text{HNO}_3$  two or three times. Add 20 ml. of water, boil and filter. Reject the residue of  $\text{SiO}_2$ . Collect the filtrate in a 400 ml. beaker.

Add a few drops of phenolphthalein indicator solution. The solution is coloured pink. Add dil.  $\text{HNO}_3$  (1:1) until colorless. Heat the solution to boiling. The pink colour reappears. Destroy the pink colour by the addition of dil.  $\text{HNO}_3$  (1:1). Repeat boiling and addition of dil.  $\text{HNO}_3$  until not more than 1 to 1.5 ml. of 4 N- $\text{HNO}_3$  is consumed in rendering the solution colourless. This manipulative procedure has for its object the securing of a solution which is feebly alkaline. It is in such a medium that  $\text{Ag}_3\text{PO}_4$ ,  $\text{Ag}_2\text{CrO}_4$ , etc., is precipitated by  $\text{AgNO}_3$  solution. Add this solution in slight excess. Filter off the ppt., add a slight excess of  $\text{NaCl}$  solution to react with the excess of  $\text{AgNO}_3$ . Boil. Filter off  $\text{AgCl}$ , wash the ppt. with water, collecting the filtrate and washings in a 400 ml. beaker. Add 0.106 gm.  $\text{Na}_2\text{CO}_3$  in the form of a 2 normal solution. Heat to boiling. Now add a solution of  $\text{CaCl}_2$  (N) until no further precipitation takes place. Let stand for half to one hour. Filter, wash and ignite the paper with the

residue in a platinum crucible over a Bunsen burner. Cool. The ppte. is  $\text{CaF}_2 + \text{CaCO}_3$ . Dissolve in 1-2 ml. of *N*-acetic acid in the crucible itself. Dilute with hot water, filter and wash with hot water. Ignite the filter paper with the residue of  $\text{CaF}_2$  in a platinum crucible over a Bunsen burner. Cool and weigh. Check the %  $\text{CaF}_2$  by conversion into  $\text{CaSO}_4$  by heating to fuming with conc.  $\text{H}_2\text{SO}_4$  ( 1 to 2 ml. ) twice and by final strong heating over a Bunsen burner.

The elimination of phosphoric acid as  $\text{Ag}_3\text{PO}_4$  is necessary before the sodium and potassium fluorides are precipitated by the addition of  $\text{CaCl}_2$ . Fluorspar may or may not contain phosphate but in dealing with samples of fluorapatite the above procedure is necessary. KF is much more soluble in water than NaF.

## EXPERIMENT 75.

### Complete Analysis of Fire Clay.

#### Moisture :—

Reduce to a fineness of 20 mesh sieve the sample of fireclay. Weigh 3 gms. of this into a silica crucible, dry at  $100^\circ\text{C}$ . for 2 hours in a steam oven, cool and reweigh. Difference yields moisture.

#### Loss on Ignition :—

Place the crucible and contents after making a determination of the moisture in a sample, in a muffle furnace ( temp.  $950^\circ\text{C}$ . ) and heat for 10 mins. with the cover on. Remove the cover and continue to heat for 50 mins. more. Cool in a desiccator and weigh. The loss in weight represents combined water and organic matter. Calculate these on the basis of the moisture-free sample.

**Silica :—**

Grind the material from the above until it passes completely a 180 mesh sieve. Ignite for a few minutes to expel any moisture absorbed during the grinding. Cool in a desiccator and weigh out 0.3 gm. sample of the material into a platinum crucible. Introduce 5 gms.  $\text{Na}_2\text{CO}_3$  into the same. Mix and fuse for 30 minutes over the blast lamp or a muffle furnace, preferably the latter. Cool. Extract melt with water and then with dil. HCl s.g. 1.1 as shown under Expt. 66. Evaporate to dryness. Bake at  $110^\circ\text{C}$ . for 4 hours. Cool. Redissolve in 20 ml. dil. HCl of 1.1 s.g. by heating for about 5 minutes, filter off the silica. The filtrate still contains some silica. To separate this, evaporate to dryness and bake a second time. Cool. Take up with 5 ml. conc. HCl and 20 ml. water, filter through a separate filter-paper, wash until free from chloride, transfer both the silica residues to a platinum crucible, ignite and weigh.

Treat with 5 ml. 1 : 4  $\text{H}_2\text{SO}_4$  and 5 ml. HF. Evaporate to dryness and ignite for 5 minutes. Weigh. The loss represents  $\text{SiO}_2$ .

Fuse the residue of  $\text{TiO}_2$  in the crucible with about  $\frac{1}{2}$  gm. of  $\text{Na}_2\text{CO}_3$ , cool and extract the melt with water and add the same to the filtrate from the silica filtration.

**$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{TiO}_2$  :—**

To the combined filtrate (about 250 ml.) add 2 gm.  $\text{NH}_4\text{Cl}$  and then  $\text{NH}_4\text{OH}$  until slightly alkaline. Boil to a faint smell of  $\text{NH}_4\text{OH}$ . Filter. Wash twice with water. Redissolve the precipitate in 10 ml. dil.  $\text{HNO}_3$  of s.g. 1.2. Add  $\text{NH}_4\text{OH}$  till slightly alkaline. Boil to a faint smell of  $\text{NH}_4\text{OH}$ , stir in pulp from one ashless filter-paper of 9 cms. dia. and filter off the precipitate. Ignite in a platinum crucible, cool and weigh as  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{TiO}_2$ .

Determine each separately as follows :—

**TiO<sub>2</sub> :—**

Fuse the ignited oxides with 10 times their weight of KHSO<sub>4</sub> in a platinum crucible. Cool, extract with dil. H<sub>2</sub>SO<sub>4</sub> of s.g. 1.2. Transfer to a 250 ml. graduated flask and make up exactly to the mark. Mix. Withdraw 50 ml. by means of a pipette, introduce into a colour comparison tube. Similarly introduce into a second tube 2 ml. of standard titanium sulphate solution. Add H<sub>2</sub>O<sub>2</sub> to each and adjust tint of sample to equality of tint with the standard by dilution with water. Calculate % TiO<sub>2</sub>. See Expt. 56.

**Fe<sub>2</sub>O<sub>3</sub> :—**

Transfer the solution of the sample of TiO<sub>2</sub> from the colour tube to a 500 ml. beaker. Transfer the remainder of the solution in the measuring flask also to the same beaker.

Add 5-10 ml. of dil. HCl. Heat to boiling. Add SnCl<sub>2</sub> to reduce FeCl<sub>3</sub> to FeCl<sub>2</sub> and finish for Fe as shown in Expt. 10.

**Al<sub>2</sub>O<sub>3</sub> :—**

Obtain this by deducting the weight of Fe<sub>2</sub>O<sub>3</sub> + TiO<sub>2</sub> from the weight of Fe<sub>2</sub>O<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub> + TiO<sub>2</sub>.

**MnO :—**

Concentrate the combined filtrates from Fe<sub>2</sub>O<sub>3</sub> + Al<sub>2</sub>O<sub>3</sub> + TiO<sub>2</sub> to 200 ml. Add 25 ml. bromine water, make ammoniacal, boil for half an hour, filter off the precipitate, ignite at 900°C. and weigh as Mn<sub>3</sub>O<sub>4</sub>.

**CaO and MgO :—**

Determine these from the filtrate from the MnC determination. See Expt. 11.

**Determination of alkalies :—**

See Expt. 77. There it is fully described. This method is applied without any modification.

**NOTES :—**

(1) Materials like fire-clay, fire-brick, quartzite, silica brick, etc., having high percentages of silica do not yield the entire amount of silica by one evaporation. A second evaporation after filtering off the silica from one evaporation is necessary.

(2) The tendency of aluminium and iron hydroxides to adsorb Mn, Ca, Mg, etc. in the form of their salts is minimised by the procedure described. Also, the danger of loss of Al, Fe in the form of volatile chlorides is avoided by final precipitation from a nitric acid solution of the hydroxides.

(3) A blank for the impurities in the reagents must be run along with a sample.

The procedure for the analysis of fire-clay is applicable without modification for the analysis of materials like fire-brick, silica sand, quartzite and silica brick.

**EXPERIMENT 76.****Examination of Fire-Clay****Preparation of clay :—**

Crush two fire-bricks and powder them so as to pass a 20-mesh sieve. Similarly pass raw fire-clay through the same sieve. Mix 2 parts of the raw clay with 1 part of the burnt clay. 1 pint (269 ml.) of the former and  $\frac{1}{2}$  pint of the latter will do. Mix well. Add sufficient water to make the mixture thoroughly plastic; knead well by throwing on a wooden board and allow to stand till the next day. The plasticity and the uniformity of the clay are increased by allowing the mix-



ture to stand as long as possible and by frequent kneading. The mixture may be kept covered with a wet cloth.

### **Preparation of crucibles and crucible lids :—**

Prepare about a dozen small clay crucibles with the aid of a gunmetal or brass mould. Grease the mould and core with olive or mustard oil. Fig. 22 shows the gun-metal mould, the core, etc. used in the making of the fire-clay crucibles.

Fit the brass mould into a wooden base A. This has a small hole into which the centering-pin B of the core fits. Put enough clay to make a crucible into the mould, press the core C down, giving a rotary motion to it at the same time until the neck of the core comes down on the top of the flask. The excess clay comes out through an opening in the head of the core. It is then removed, a small piece of clay dropped in to stop the hole in the bottom, and the interior is exactly smoothed off by means of an exactly similar core but without a pin. The crucible is then removed by lifting the mould from the stand and applying slight pressure below. A few gentle taps with a small hammer are effective.

Allow the crucibles to dry in the Lab. for 2-3 days and bake in a gas muffle for two to three hours, beginning with the muffle quite cold and finishing at the highest attainable temperature. Take out from the furnace and when cold, see whether any glazing or incipient fusion has occurred, whether cracking has taken place or, if the clay is brittle or tender. Record the colour and texture of the product.

Roll out some of the prepared clay on a board with a rolling pin and cut out lids for the crucibles, dry and bake in the muffle as before.

If the edges do not show signs of being rounded off by heat, the clay may be regarded as satisfactory and and further tested as follows :—

Prepare three small square pyramids each about 1" high, one from a standard clay of good quality and the other two from the clay to be examined. When the pyramids are dry, take four small clay crucibles of good quality and in each of them place one of the pyramids which are to be tested and in the fourth, put a piece of soft steel. Mark each pyramid so as to ensure subsequent identification. Marks made on the outside with a glass-marking pencil will serve. Cover each crucible with a lid and fix the four crucibles by means of fireclay on to the narrow edge of half a fire-brick. Place in a cold wind furnace and build a fire round the crucibles. Gradually increase the heat of the furnace and maintain at the highest temperature for about an hour or more. Allow to cool. Remove the fire-brick with the crucibles. Gently tap the lids off the mouth of the crucibles and examine their contents. If the temperature was sufficiently high, the steel will have fused to a button. If the clay pyramids are covered with black spots or appear glazed, they are unsatisfactory. Freedom from these indicates good quality clay.

#### **Resistance to corrosion :—**

Prepare two crucibles one from standard quality clay and the other from the clay to be tested. Melt  $\frac{1}{2}$  oz. of ferrous silicate, litharge or black copper oxide in each of these, in the same wind furnace. Compare the effect produced in the two cases. Note the time taken for the fused material to make a hole through the side or bottom of the crucible in each case.

#### **Plasticity :—**

To obtain a quantitative value, proceed as follows:—

Pass a small quantity of the clay to be tested through a 40-mesh sieve ; mix with a suitable quantity of water and make into a rod about  $\frac{1}{4}$ " in diameter and 4" in length. Lay this on a board and bend through an angle of  $180^\circ$ . If cracking develops on the outside of the bend, the angle at which the fracture commences should be noted. Clay with moderate plasticity should not show cracks when thus bent. Mix some of the dry clay with 20%, 50% and 100% of its weight of fine sand; pass the mixture through 40-mesh sieve, and make up into rods as before. Note the proportion of sand and the angle through which the clay bends before cracks develop. The proportion of sand added is a measure of the plasticity of the clay. The more plastic clays will allow of more sand being added in these tests.

### **Shrinkage :—**

Mix the clay with sufficient water, knead it well and roll into a slab  $12 \text{ cm} \times 5 \text{ cm} \times 0.5 \text{ cm}$ . Make two marks by light scratches with a pin exactly 10 cms. apart. Measure the distance when dry and when it has been baked at different temperatures. Express the shrinkage in percentage of the original length.

### **Porosity :—**

Break off a piece of fireclay the size of a betel-nut. Dry for half an hour in a steam oven and bake in a muffle. Cool. Weigh carefully. Let this be D gms. Suspend by horse-hair in a covered beaker in water and boil for some hours to expel air. Allow to cool to room temperature while still suspended. Weigh in cold water as in taking specific gravity measurements. Let this be S gms.

$$\text{Apparent S. G.} = \frac{D}{D-S} = \frac{\text{Weight in air}}{\text{Loss of weight in water}}$$

Now take out the weighed piece, dry the outside quickly on moist filter paper or a piece of moist cloth and weigh in air to get the weight when the pores are filled with water. Let this weight be  $W$  gms. The pore space equals  $W - D$  ml.

The apparent porosity is  $\frac{W - D}{W - S} \times 100$

### EXPERIMENT 77.

#### Determination of $K_2O$ and $Na_2O$ in Felspar.

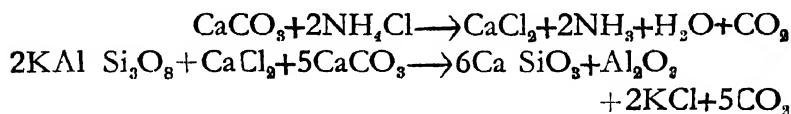
##### Method of J. Lawrence Smith.

##### Principle:—

When an intimate mixture of ammonium chloride, calcium carbonate and the finely powdered felspar is heated very gently in a platinum crucible, calcium chloride is formed. On raising the crucible to a red heat, the calcium chloride fuses and reacts with the felspar, forming  $KCl$ ,  $NaCl$ ,  $CaO$ ,  $CaSiO_3$ ,  $Al_2O_3$ ,  $Fe_2O_3$ , and  $MgO$ . Of these the three first only are soluble in water. By treating the cold sintered mass in the crucible with water and filtering the solution,  $KCl$ ,  $NaCl$ ,  $CaO$  and a small quantity of  $CaCl_2$  pass into the filtrate. The last two are precipitated as  $CaCO_3$  by the addition of  $NH_4OH$  and  $(NH_4)_2CO_3$ . The small quantity of  $CaCO_3$  still left in solution is precipitated by  $(NH_4)_2C_2O_4$  as  $CaC_2O_4$ . The filtrate consisting of the alkali chlorides is evaporated to dryness and cautiously ignited to destroy the excess of ammonium salt added as precipitant. The ignited residue consisting of the chlorides of  $Na$  and  $K$  is weighed. This is then dissolved in water and treated with chloroplatinic acid. Both the chlorides are changed into chloroplatinates. Of these only the sodium salt is soluble in alcohol of 0.86 specific gravity. The insoluble potassium chloroplatinate is obtained as residue on the

filter-paper when the liquid containing the two chloroplatinates is filtered. This residue is dissolved in hot water, the solution evaporated to dryness in a platinum dish and the residue weighed. From the weight of  $K_2PtCl_6$  that of  $KCl$  is calculated. This is deducted from the weight of the total chlorides. The difference is the weight of  $NaCl$ . From the weights of the chlorides, the percentages of the respective oxides are calculated.

The reactions that take place when the mineral is heated with  $NH_4Cl$  and  $CaCO_3$  may be represented as follows:—



### Procedure:—

Weigh about 0.5 gm. of ammonium chloride and exactly 0.5000 gm. of the finely powdered mineral into an agate mortar. Grind the two by means of the pestle so that they are intimately mixed. Weigh 4 gms. of the purest precipitated chalk. Add about 2 gms. of this to the contents of the mortar. Mix thoroughly by grinding with the pestle. Transfer the mixture without loss by means of a horn spatula into a 30 ml. capacity platinum crucible. Rinse the mortar and the pestle two times with small quantities of the weighed calcium carbonate left over and finally transfer the remaining  $CaCO_3$  to the crucible. Cover with a lid and heat over a very low flame for about 10-15 minutes so that ammonia is just smelt at the mouth of the crucible. Turn the gas fully on and raise the lower three-fourths of the crucible to redness and maintain it in this condition for an hour. Cool the crucible and contents. Transfer to a 5" porcelain dish. Dissolve any residue sticking to the crucible with hot water and

transfer to the dish. Add to it about 75 ml. of water. Keep the contents at a boil for about  $\frac{1}{2}$  hour replacing the water lost by evaporation. Press any hard lumps with an agate pestle or the flattened end of a glass rod. Allow to settle. Decant through a 9 cm. filter paper, collecting the filtrate in a 600 ml. beaker. Boil again with 50 ml. more of water. Allow to settle and decant. Repeat three times. Wash with water the filter-paper and the residue 6 or 7 times so as to free them from chlorides. The filtrate will amount to about 300 ml. when this has been accomplished. Add to it a solution of ammonium carbonate (about 2 gms. in 25-30 ml. of water) and a few drops of ammonia. Boil for two or three minutes. Allow to settle. Filter into a large evaporating dish (6" diameter) and wash the precipitate and paper three or four times. Evaporate the filtrate to dryness and gently ignite to destroy the excess of ammonium salts. Cool. Dissolve the residue in water. Filter into a 100 ml. beaker. Add a few drops of a saturated ammonium oxalate solution to the boiling liquid in the 100 ml. beaker. Allow to settle for 24 hours the precipitate of calcium oxalate that forms. Filter through a small filter-paper (7 cm. dia.) into a weighed 100 ml. capacity platinum dish. Evaporate to dryness on the hot plate or better on a water-bath. Gently ignite to destroy the excess of ammonium oxalate. Cool. Moisten with a few drops of dil. HCl. Again heat gently to drive off the excess of HCl. Raise to a dull red heat. Cool in the desiccator and weigh. The increase in the weight of the dish represents the weight of the chlorides of sodium and potassium.

To determine the amount of KCl, proceed as follows :—

Dissolve the chlorides in the platinum dish in 6-7 ml. of water, add a few tenths more than the calculated

number of millilitres of  $\text{H}_2\text{PtCl}_6$ . The calculation is based on the assumption that the weight of the chlorides obtained is entirely  $\text{NaCl}$ . Evaporate nearly to dryness on a simmering water-bath. Cool. Add a few ml. of 0.86 s. g. alcohol. Break up any crust with a short glass rod into fine powder. Fit a 7 cm. filter paper to a small funnel, moisten the paper with the alcohol, decant the liquid through the paper, repeat the treatment with alcohol and the decantation until the liquid runs through the filter-paper colorless and the residue in the dish shows no orange-coloured particles and is a pure golden yellow. Transfer it to the filter-paper, allow the alcohol to drain completely. Wash the edge of the filter-paper with the alcohol dropped from a dropping bottle. Dissolve with hot water the residue on the paper and collect the solution in a weighed platinum dish holding the bulk of  $\text{K}_2\text{PtCl}_6$ . Evaporate to dryness on a water-bath. Heat in the air-oven at  $120^\circ\text{C}$ . Cool in the desiccator and weigh. Convert the weight of  $\text{K}_2\text{PtCl}_6$  to  $\text{KCl}$ . Deduct from the weight of the combined chlorides. Reduce each to the oxide.

The reagents used must be run for the amounts of alkalies contained in them. The weights of reagents used for this run known as the 'blank run' must be equal to those used in the sample run and the volume of distilled water used must also be nearly equal to that in the sample run.

Notes :—

(1) In detaching the sintered mass from the crucible considerable difficulty will be caused if the temperature maintained much exceeds  $900^\circ\text{--}920^\circ\text{C}$ . Should there be difficulty in detaching the mass from the crucible, even when it has been maintained within this range of temp-

erature, the experiment must be re-started and a gram more of calcium carbonate used.

(2) As the alkali chlorides volatilise slightly, it is preferable to condense the vapours by standing a porcelain crucible filled with water on the platinum lid. The alkali chlorides are thus condensed on the lower surface of the lid.

(3) As the precipitate of  $\text{CaCO}_3$  occludes small quantities of  $\text{NaCl}$  and  $\text{KCl}$ , it is advisable to dissolve the precipitate in dil  $\text{HCl}$ , and re-precipitate the calcium as  $\text{CaCO}_3$  by adding  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$ . The precipitate is filtered off, the filtrate added to the main filtrate and the remaining operations then proceeded with. Ammonium carbonate dissolves slowly in water. The crystals must be powdered and left in contact with *cold* water for an hour or so to obtain a solution.

(4) The ignition of the contents of the porcelain dish to destroy the ammonium salts must be very cautiously carried out. It is best not to heat the dish at the bottom, which will lead to loss by spirting. Heat from the side beginning at the top by moving the flame to and fro and gradually directing it to the bottom. This manipulation is effected by holding the lighted burner in the hand. Ignition of the platinum cup and contents must be similarly carried out. It must not be heated to bright red as the alkali chlorides will slightly volatilise.

(5) Owing to the high cost of the chloroplatinic acid reagent, only a few tenths more than the calculated number of ml. must be added for precipitating the chloroplatinate of potassium.  $\text{K}_2\text{PtCl}_6$  will not appear as a precipitate until the solution is concentrated by evaporation. Both  $\text{K}_2\text{PtCl}_6$  and  $\text{Na}_2\text{PtCl}_6$  are formed on concentration of the solution. Of these,  $\text{Na}_2\text{PtCl}_6$  is soluble in alcohol of .0.86 s. g., while  $\text{K}_2\text{PtCl}_6$  is insoluble. Alcohol

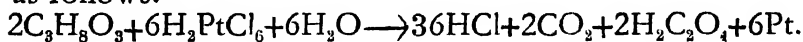


of this specific gravity is prepared by mixing 5 volumes of ordinary 95% alcohol with one volume of water.

(6) Alcohol stronger than 80% ( i. e. ) of s. g. lower than 0.86, decomposes  $\text{Na}_2\text{PtCl}_6$ , precipitating  $\text{NaCl}$ . Alcohol which is less than 75% strong ( i. e. ) of higher specific gravity than 0.86 dissolves appreciable amounts of  $\text{K}_2\text{PtCl}_6$ .

(7) The filtrate obtained by filtering off  $\text{K}_2\text{PtCl}_6$  and the residue of  $\text{K}_2\text{PtCl}_6$  contain all the platinum introduced as  $\text{H}_2\text{PtCl}_6$ . These must be accumulated and the platinum recovered. The following is the method for the recovery of platinum from residues:—

Evaporate to dryness in a porcelain dish. Take up residue in water ; pour this extract into sodium hydroxide solution of 1.2 s. g. containing 8% glycerol. Heat the liquid to boiling. Platinum is precipitated as a black powder during the process. The reaction is represented as follows:—



Filter. Wash the powder on the filter paper with water, dil  $\text{HCl}$  (s. g. 1-1) and finally with water until the filtrate is free from chloride. Dry the paper. Ignite to destroy any organic matter. Weigh and transform into  $\text{H}_2\text{PtCl}_6$  by treatment with aqua regia in a 100 ml. beaker. Repeatedly evaporate ( 6 times ) to low bulk with conc.  $\text{HCl}$  to get rid of  $\text{HNO}_3$ . Make up with water so that the solution has 10 gms.  $\text{Pt}$  per 100 ml. of solution. Care must be taken during the evaporation to see that no dry salts appear on the sides of the beaker.

(8) The method described is available for the determination of alkalis in such materials as fire-clays, fire-bricks, coal-ash, etc. ; only in these cases, 1 gm sample with proportionate amounts of  $\text{NH}_4\text{Cl}$  and  $\text{CaCO}_3$  is to be used, as the alkali content of these materials is generally very low.

(9) Owing to the high cost of platinum, perchloric acid is finding increasing application in the separation of potassium from sodium. The principle and the method are described below.

**Principle :—**

The separation of K from Na depends upon the insolubility of  $\text{KClO}_4$  in 97% alcohol. Ammonium salts and sulphates must not be present on account of the difficult solubility of ammonium salts and sodium sulphate in alcohol.

**Reagents required :—**

(1) 97% alcohol by volume. Add 3 ml. of water to 100 ml. pure alcohol. Mix well.

(2) To 100 ml. of 97% alcohol, add 0.2 ml. of  $\text{HClO}_4$  of s.g. 1.12.

**Procedure :—**

Obtain the alkalis as chlorides in the manner shown above. Dissolve in 15-20 ml. water. Add 5 ml. of 20%  $\text{HClO}_4$ . Evaporate on a water-bath to a syrup, add a little water and continue evaporation with constant stirring until white fumes appear. If no fumes appear, add a little more  $\text{HClO}_4$  until heavy fumes of  $\text{HClO}_4$  appear. Cool and stir with 20 ml. of Solution No. 2. The crystals should be broken up somewhat before decanting through a Gooch crucible with asbestos felt. Prepare this for use as shown in Expt. 78A. Decant the solution containing the crystals of  $\text{KClO}_4$  through the Gooch crucible. Wash them by decantation twice with Solution No. 2. Transfer the residue to the felt, wash with the above alcoholic solution 3 to 4 times and finally only with 97% alcohol. Dry at  $130^\circ\text{C}$ . and weigh as  $\text{KClO}_4$ .

**Preparation of Perchloric Acid :—**

Heat in a round-bottomed flask 100-200 gms. of commercial  $\text{NaClO}_3$  until oxygen begins to be evolved

slowly. Maintain this temperature until the mass becomes solid (about  $1\frac{1}{2}$ -2 hrs), which now consists of  $\text{NaClO}_4 + \text{NaCl}$ . Cool, dissolve the melt in water, add  $\text{HCl}$  to decompose any  $\text{NaClO}_3$  still remaining and evaporate to dryness with constant stirring. Break up the dry mass, transfer to a large size beaker, add conc.  $\text{HCl}$ . By this  $\text{HClO}_4$  is formed and solid  $\text{NaCl}$  separates out. Filter through a Gooch crucible with asbestos felt; wash the crystals by decantation twice with conc.  $\text{HCl}$ .

Evaporate filtrate on a water-bath until  $\text{HCl}$  is expelled and heavy white fumes of  $\text{HClO}_4$  begin to be evolved.

In case there is a potassium salt contaminating the sodium chlorate used, proceed as follows:—Dissolve the cold melt in 97% alcohol, filter off the precipitate through a Gooch crucible with asbestos felt, distil off the alcohol from the filtrate, evaporate to dryness and then continue the operations described above.

NOTE : --

Mixture of alcohol and perchloric acid should not be heated over a bare flame as a dangerous explosion is likely to result.

#### EXPERIMENT 78 A

#### **Determination of Manganese in Ferro-Manganese (Method of Ford and Williams).**

##### **Principle :—**

When to a solution of manganous nitrate containing an excess of conc.  $\text{HNO}_3$ , potassium chlorate is added,  $\text{MnO}_2$  is precipitated. This is filtered off through asbestos, the precipitate with the asbestos felt is treated, in the presence of sulphuric acid, with a measured excess of standard oxalic acid, the mixed solutions heated up to about  $70^\circ\text{C}$ . and the excess of oxalic acid

determined by titration with standard  $\text{KMnO}_4$ . From the number of ml. of oxalic acid used up, the percentage of Mn is calculated.

**Solutions required:—**

1. Dil.  $\text{HNO}_3$  s.g. 1.2.
2. Standard Potassium Permanganate solution. The same as in Experiment 8.
3.  $N/10$  oxalic acid. Described below.

**Procedure:—**

Weigh a 0.3–0.4 gm. sample of the alloy into a tall 400 ml. beaker. Add 30 ml. dil.  $\text{HNO}_3$  (s.g. 1.2). Place on the hot plate. When completely dissolved, add 60 ml. conc.  $\text{HNO}_3$ , cool to room temp. and then introduce cautiously 6–7 gms.  $\text{KClO}_3$  crystals. Continue heating on the hot plate for 15–20 minutes. Remove from the plate, dilute with hot water to about 100 ml., filter through a Gooch crucible containing asbestos felt, wash with hot water until free from ferric salts and  $\text{HNO}_3$ . Transfer the crucible with the felt of asbestos and precipitate to a 300 ml. capacity porcelain dish, add 150 ml. of  $N/10$  oxalic acid by means of a 50 ml. pipette, 40 ml. dil.  $\text{H}_2\text{SO}_4$  (s.g. 1.20), heat to  $70^\circ\text{C}$ ., stir well, lift the crucible from the solution by means of a glass rod and wash it with water. Stir the contents of the dish with a glass-rod until no brown particles are seen. Run from a burette standard  $\text{KMnO}_4$  solution into the dish until a pink colour is obtained.

The following data on a sample run will illustrate the method of calculation:—

Weight of sample	=0.2698 gm.
Weight of tube+ oxalic acid	=10.5000 gms.
Weight of same after transfer of part of the acid crystals into a beaker	} =8.0000 gms.

This weight was dissolved in water and the solution made to about 500 ml.. Volume of oxalic acid introduced to react with  $\text{MnO}_2$  ( run from a 100 ml. burette ) = 145.5 ml.

Volume of  $\text{KMnO}_4$  used up to react } = 55.0 ml.  
with the excess oxalic acid

Strength of  $\text{KMnO}_4$  solution used = 0.8872N/10

Titration values to fix the strength of oxalic acid:—

Oxalic	Permanganate
20.1 ml.	19.4 ml.
55 ml. $\text{KMnO}_4$	=56.89 ml. oxalic acid
Volume of oxalic acid used } for reducing $\text{MnO}_2$ to $\text{MnO}$ }	=145.5 ml. - 56.89 ml. =88.61 ml.

Strength of oxalic acid =  $\frac{19.4}{20.1} \times .8872 \text{ N/10}$

88.61 ml. of .8582 N/10 } = 88.61 ml. of .8582  
oxalic acid } N/10  $\text{MnO}_2$

$$= \frac{.8582 \times 88.61 \times 55}{2 \times 10 \times 1000} \text{ gm. Mn.}$$

0.2698 gm. sample contains  $\frac{0.8582 \times 88.61 \times 55}{2 \times 10 \times 1000}$  gm. Mn

100 gms.        "        "         $\frac{0.8582 \times 88.61 \times 55 \times 100}{2 \times 10 \times 1000 \times 0.2698}$   
= 77.5 gms. Mn.

i. e. 77.5% Mn.

NOTES:—

(1) The sample of ferro-manganese must be extremely finely powdered. It must pass through a 100 mesh sieve. Solution of the sample is easily effected only by grinding the coarsely powdered sample to this degree of fineness in an agate mortar.

(2) The nitric acid used must be free from nitrous acid, as this has a reducing action on the manganese dioxide formed. Such acid is 'obtained' by bubbling

air through 200 ml. of the Bench-Reagent for 15–20 minutes. The arrangement of apparatus is as shown in Fig. 11. The gas wash-bottle contains the acid.

(3) Due to the variation of the composition of the precipitate formed, it is desirable to fix the strength of the oxalic acid solution in terms of Mn content by the above process.

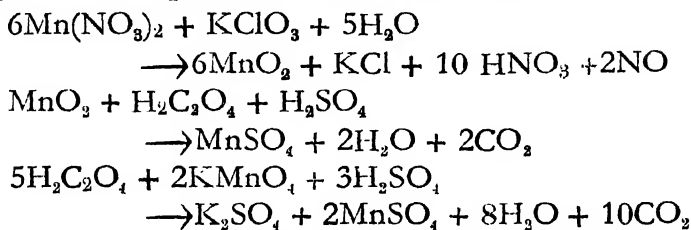
(4) Filtration through filter paper is not feasible as the same will be destroyed by the strongly acid liquid containing the precipitate. Very large dilution with water, while serving to dilute the acid, tends to dissolve some of the precipitate. The asbestos filter is prepared as follows :—

Some long fibered soft asbestos is cut with a pair of scissors into  $\frac{1}{2}$  cm. length pieces and the cut pieces digested with 30–40 ml. of conc. HCl in a basin in a boiling water-bath. The asbestos is then filtered off on a Buchner funnel and washed with distilled water until free from chloride. A small flock of the material is shaken vigorously with about 200 ml. water in a flask. The asbestos distributed in flakes through the water is poured on to a Gooch crucible fitted to a filter flask, the latter being connected through a second filter flask to the Laboratory Bunsen filter pump. A thickness of asbestos layer of about 2 mm. is sufficient. When the water after each filling of the crucible is drained, light pressure with the flattened end of a glass rod is applied. Beginners commonly make the mistake of forming a very thick layer of asbestos and applying great pressure while packing. Such procedure defeats one of the purposes for which this method of filtration is adopted, namely, rapidity. When the Gooch crucible with the asbestos is required for gravimetric work, it must be dried and ignited at a temperature which will be employed in the determination. It is then weighed,

The process of washing the asbestos felt in the crucible is repeated. It is heated, cooled and weighed. The crucible filter is considered fit for use if the loss in weight is not more than 0.0001 gm.

(5) When HCl is employed to bring the sample into solution, the excess of it must be got rid of by repeated evaporation to low bulk with conc.  $\text{HNO}_3$  before the crystals of  $\text{KClO}_3$  are added. Otherwise an explosion leading to loss of the substance by spirting will result.

(6) The reactions that take place at the different stages of the experiment are as follows:—



(7) For the determination of manganese in ores, this method may also be employed in place of Volhard's method, described in Experiment 58. In this case, preliminary treatment with HCl is necessary, as the ore is insoluble in dil. or conc.  $\text{HNO}_3$ . Both the methods consume about the same length of time.

(8) When the precaution of freeing the nitric acid from the reducing oxides of nitrogen has not been taken, manganese will be found in the filtrate from  $\text{MnO}_2$ :— $\text{N}_2\text{O}_3 + \text{MnO}_2 \rightarrow 2\text{NO}_3 + \text{MnO}$ .  $\text{MnO}$  dissolves in  $\text{HNO}_3$ . To determine its amount the filtrate is made up to a known volume and the manganese in an aliquot part determined by the persulphate method. The results obtained may be added to the percentage obtained by the Ford-Williams' Method.

(9) It is recommended that the addition of potassium chlorate be made to a cold solution as the precipi-

tate of  $\text{MnO}_2$  formed under the above condition is readily soluble on treatment with oxalic acid-sulphuric acid mixture.

### EXPERIMENT 78 B.

#### Determination of Chromium in Ferro-Chrome.

##### Principle :—

The alloy is fused with  $\text{Na}_2\text{O}_2$  in a pure iron crucible when sodium chromate is formed. This is acidified with dil.  $\text{H}_2\text{SO}_4$  and then treated with an excess of ferrous ammonium sulphate either in the form of the crystals or in the form of a standard solution. The excess of the reducing agent is titrated against 0.1 N- $\text{KMnO}_4$  solution.

##### Procedure :—

A 0.5000 gm sample crushed to pass through a 420 micron ( 1 micron =  $\frac{1}{0.001}$  mm. ) sieve in the case of the low carbon alloy and a 149 micron sieve in the case of the high carbon alloy is used.

Weigh about 8 gms. of  $\text{Na}_2\text{O}_2$  into a 30 ml. capacity iron crucible. Introduce the half gm. sample into it. Stir well by means of an iron nail. Scrape off any material adhering to the stirrer by means of another nail. Cover with a 2 gm. layer of  $\text{Na}_2\text{O}_2$ . Fuse either over a Bunsen burner or in an electric muffle at 600-700° C. Maintain the mass in a molten condition for 7-10 minutes. Grip by means of a pair of steel tongs and rotate the crucible so that any unattacked material creeping to the top of the side is brought into contact with the molten liquid. Cool. Introduce the crucible into a 600 ml. capacity beaker containing about 150 ml. of water. When the melt has dissolved, remove the crucible from the beaker with the pair of tongs and rinse both the crucible and the tongs with water.



Add 60 ml. of dil.  $\text{H}_2\text{SO}_4$  (1:1) and 5 ml. of conc.  $\text{HNO}_3$ . Boil the solution for about 15 minutes. Add 10 ml. of a 0.5%  $\text{AgNO}_3$  solution and 4 to 5 drops of a 2.5%  $\text{KMnO}_4$  solution. Follow this up with a 5 gm. addition of ammonium persulphate. Boil for 10 minutes. All the chromium and the manganese, if any, will now be in their highly oxidised state. It is necessary to destroy the permanganic acid before reducing the chromic acid. For this purpose introduce 4 gms.  $\text{NaCl}$  dissolved in about 40-50 ml. of water. Boil to dissolve off any precipitate of  $\text{MnO}_2$  and continue to boil for 10 minutes after the last particles of  $\text{MnO}_2$  have disappeared. Cool to room temp. Add 3 to 5 ml. of conc. orthophosphoric acid. Dilute to 300-350 ml. Add an exactly weighed amount (about 8 gms.) of ferrous ammonium sulphate. Stir until well dissolved. Add from a burette 0.1 N- $\text{KMnO}_4$  until the clear green colour of the chromic sulphate becomes darkened.

$$1 \text{ ml. } 0.1 \text{ N-}\text{KMnO}_4 = 1 \text{ ml. } 0.1 \text{ N-}\text{FeSO}_4 \\ = 0.001734 \text{ gm. Cr.}$$

Calculation.—In a determination using a 0.5 gm sample of the alloy, 8 gms. of  $\text{FeSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $6\text{H}_2\text{O}$  were added and the excess of it required 14.8 ml. of 0.1 N- $\text{KMnO}_4$ .

8 gms. of the salt are equal to an addition of 204.1 ml. 0.1 N- $\text{KMnO}_4$ .

The chromate consumed  $204.1 - 14.8$  ml. of 0.1 N- $\text{FeSO}_4$ .

Hence % chromium equals  $189.3 \times .001734 \times 100 \div 0.5 = 65.96$ .

## EXPERIMENT 78 C.

### Determination of Silicon in Ferro-Silicon

#### Principle :

The finely powdered alloy is opened out by a fusion attack with sodium peroxide in an iron crucible. So-

dium silicate results from the fusion. This is evaporated to dryness with HCl, redissolved in HCl, filtered and the residue ignited and weighed as impure  $\text{SiO}_2$ . This is treated with  $\text{H}_2\text{SO}_4$  and HF and the residue weighed. Difference gives the amount of pure silica from which silicon is calculated.

**Procedure :—**

Weigh a 0.5 gm sample of the alloy passing through a 100 mesh sieve (149 micron) into a 50 ml. iron crucible containing about 8 gms. of  $\text{Na}_2\text{O}_2$ . Stir with an iron nail. Scrape off any adhering material with a stainless steel spatula. Cover the mixed mass with an additional layer of about 2 gms. of  $\text{Na}_2\text{O}_2$ . Heat over a low Bunsen burner flame for a few minutes, holding the crucible with a pair of tongs. Gently rotate so that the molten liquid comes into contact with particles that may have crept to the top of the crucible. Maintain the bottom of the crucible at a dull red heat for 5 minutes. Violent heating at the start leads to loss of material. Therefore avoid doing so.

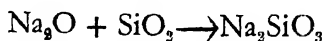
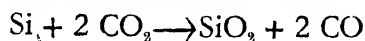
Tap the crucible when the mass has solidified, but is still hot, on an iron plate so as to dislodge the cake from the crucible. Transfer to a nickel dish of about 300 ml. capacity or to a 600 ml. pyrex beaker. Add 50 ml. of cold water. When reaction ceases, dissolve the contents of the crucible with a little water and transfer the solution to the beaker. Rinse the crucible 2 or 3 times with water. Add the rinsings to the beaker. Now transfer the solution from the beaker to a casserole, add 40-50 ml. conc. HCl so as to have an excess of acid. Evaporate to dryness at a temp. not exceeding  $110^\circ\text{C}$ . Bake. Cool, redissolve in 20 ml. of conc. HCl by heating gently for 2-3 minutes. Dilute with 250 ml. of hot water, and filter through a 11 cm. filter paper containing a little ashless paper pulp. Wash, un-

til free from iron salts alternately with dil. HCl (1 : 10) and hot water. Finally wash with hot water. Reserve the paper with the residue.

Evaporate the filtrate to dryness a second time and bake for 1 hr. at a temp. not exceeding 110°C. Cool. Add 20 ml. of 1 : 1 HCl, heat to boiling, dilute with 200 ml. hot water and filter. Wash as above, first with dil. HCl (1 : 10) and finally with water. Transfer both the residues with the filter papers to a large size platinum crucible and ignite first gently and then strongly over a blast lamp. Cool in a desiccator and weigh. Ignite a second time, cool and weigh to see if the weight is constant. Adopt the hydrofluorisation treatment described in Expt. 66 pp. 378-379. Use about 8-10 ml. of HF.

NOTES :—

1. An alternative method of opening out the alloy consists in heating the sample (about 0.5 gm.) in a platinum crucible with a mixture consisting of 2 parts by weight of  $\text{Na}_2\text{CO}_3$  and one part by weight of  $\text{MgO}$ . This mixture is sometimes known as Rothe's mixture. The reactions taking place are :—



The weight of finely powdered sample to be taken for analysis is the same as in the above method, an intimate mixture being secured by grinding together 0.5 gm. of the sample and 6-8 gms. of Rothe's mixture. Heating over a Teclu burner is conducted for about an hour. The mass when cold is transferred to a large size casserole, treated with 40 ml. of conc. HCl and evaporated to dryness and baked. The further details are the same as above.

2. A blank for the silica resulting from the attack of the reagents employed on the glass and porcelain vessels must be determined. Also a blank for any residue in HF must be run using the same volume as in the experiment.

### EXPERIMENT 78 D.

#### Determination of Vanadium in Ferro-Vanadium.

##### Principle :—

The alloy is opened out with a mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . The vanadyl sulphate is oxidised to vanadic acid by  $\text{KMnO}_4$  which at the same time oxidises the organic matter present. The vanadic acid is reduced by excess of ferrous sulphate, the excess eliminated by ammonium persulphate and the vanadyl sulphate finally oxidised by a standard solution of  $\text{KMnO}_4$ .

**Procedure :—**Weigh into a 600 ml. beaker a 0.5 gm. sample of the crushed alloy. Add 60 ml. dil.  $\text{H}_2\text{SO}_4$  (1:2) and 25 ml. dil.  $\text{HNO}_3$  (1:1), heat on the hot plate to copious fumes of  $\text{SO}_3$ . Cool to  $15^\circ\text{C}$ . Add 300 ml. of water. Add 0.1 N— $\text{KMnO}_4$  until a very strong pink colour persists. Add 0.1 N—ferrous ammonium sulphate until the permanganate colour is destroyed and excess of ferrous iron is present. Test for this on a spot plate using a drop of a 0.1% solution of potassium ferricyanide. Add 10 to 15 ml. of a freshly prepared 10% ammonium persulphate solution and stir vigorously for one minute. This will oxidize the excess of ferrous iron leaving the vanadyl sulphate unaffected. Now add 0.1 N— $\text{KMnO}_4$  with constant stirring until a faint pink colour persists for one minute. Run a blank using 0.5 gm. of iron and treating it in exactly the same way as the sample. Subtract the blank and calculate the % of vanadium.

1 ml. of 0.1 N— $\text{KMnO}_4$  = 0.0051 gm V.

## EXPERIMENT 78 E.

**Ferro-Molybdenum.****Determination of Molybdenum.****Principle :—**

The alloy is opened out with a mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . The silica is filtered off. The filtrate is neutralised with ammonia to the appearance of a faint red colour when it is poured into  $\text{NH}_4\text{OH}$ . The ppt. consisting of a mixture of  $\text{Fe}(\text{OH})_3$ ,  $\text{FeAsO}_4$ ,  $\text{FePO}_4$  etc., is filtered off and the filtrate is treated with tartaric acid followed by  $\text{H}_2\text{SO}_4$ . On passing  $\text{H}_2\text{S}$  through the solution,  $\text{MoS}_3$  and  $\text{CuS}$  separate out. These are filtered off, dissolved in a mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , oxidised with  $\text{KMnO}_4$  and the copper separated out as metal by means of zinc and filtered. The filtrate is passed through the Jones reductor and the reduced molybdenum oxidised to  $\text{MoO}_3$  by 0.1 N- $\text{KMnO}_4$ .

**Procedure :—**

Weigh a 0.5 gm. sample into a 150 ml. beaker, with a cover glass, introduce 10 ml. of dil.  $\text{HNO}_3$  (1:3), place the cover in position and heat gently until dissolved. Add little by little 10 ml. of dil.  $\text{H}_2\text{SO}_4$  (1:1) and evaporate to fumes of  $\text{SO}_3$ . Cool. Dilute to about 50 ml. Heat until the soluble salts are in solution. Rinse the cover glass with water and add the rinsings to the beaker. Filter off the silica and receive the filtrate in a 400 ml. beaker. Wash with water 4 or 5 times, then with 6 N- $\text{NH}_4\text{OH}$  and finally with water. Neutralise the filtrate with  $\text{NH}_4\text{OH}$  until a ppt. which slowly dissolves appears. Pour this mixture into 75 ml. of nearly boiling hot ammonia of 0.96 s.g. contained in a 600 ml. beaker. Rinse the original beaker with a little water and add the rinsing to the 600 ml. beaker. Do this twice. Give a final rinsing with hot 3 N-ammonia,

adding the rinsing to the main solution. Filter through a pulp pad and wash the residue with hot water. Collect the filtrate and the washings in a 600 ml. beaker. Reserve the filtrate. Redissolve the ppte. consisting of a mixture of  $\text{FePO}_4$ ,  $\text{FeAsO}_4$  and  $\text{Fe}(\text{OH})_3$  in dil.  $\text{H}_2\text{SO}_4$  ( 1:3 ), nearly neutralise the excess acid with  $\text{NH}_4\text{OH}$  ( 1:3 ) and pour into boiling hot  $\text{NH}_4\text{OH}$  ( 1:3 ), boil for a minute and filter. Add the filtrate to the first filtrate. This process of double precipitation has for its object the recovery of any molybdenum adsorbed by  $\text{Fe}(\text{OH})_3$ . Stir in 3 gms. of tartaric acid. Saturate with  $\text{H}_2\text{S}$  and add dil.  $\text{H}_2\text{SO}_4$  ( 1:1 ) until the acid is present in excess, at the rate of 10 ml. per 200 ml. volume of the solution. Heat to boiling and let stand for 15 minutes at a temp. of about  $40^\circ\text{C}$ . Filter and wash the sulphides of molybdenum and copper with  $\text{H}_2\text{S}$  water containing 10 gms. of tartaric acid per litre of the solution. Reserve the filtrate. This may contain a small amount of molybdenum. It is to be determined colorimetrically and the amount added to that obtained from the sulphide ppte.

Treat the mixed precipitates in the beaker in which the precipitation was made with 6 ml. conc.  $\text{H}_2\text{SO}_4$  and 10 ml. conc.  $\text{HNO}_3$ . Heat until fumes of  $\text{SO}_3$  are evolved. Cool. Add  $\text{HNO}_3$ , wash down the sides of the beaker and again heat to fumes. Repeat until the solution is free from yellow colour indicating that all the organic matter is removed. Cool. Rinse the side of the beaker and add a nearly normal solution of  $\text{KMnO}_4$  drop by drop to the persistence of a pink colour. Evaporate to fumes. Cool. Add 75 ml. of water. Raise to a boil. Precipitate the copper by the addition of 2 gms. of pure granulated zinc. Continue boiling for 2-3 minutes. Filter and wash the residue with water. Receive the filtrate in a beaker. Cool to about  $40-50^\circ\text{C}$ .

Pass this filtrate through the Jones reductor and collect the liquid leaving the reductor in a mixture of ferric sulphate and phosphoric acid. For further details of the process, see Expt. 34, page 187. For the determination of molybdenum in the filtrate from the  $\text{MoS}_3$  and  $\text{CuS}$  precipitate, proceed as follows :—Boil down to a volume of 75 ml. Add 1-2 gms. of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and boil for 1 or 2 minutes. Cool. Make up to 100 ml. in a 100 ml. graduated flask. Withdraw 5 ml. by means of a 5 ml. pipette, introduce into a colour comparison tube, add  $\text{SnCl}_2$  and  $\text{KCNS}$  solution. Compare the colour intensity with that obtained by the use of a standard molybdate solution. For details see Expt. 33, page 180.

NOTES :—

(1) The addition of  $\text{NH}_4\text{OH}$  wash liquid at the first stage when filtering off  $\text{SiO}_2$  has for its object the carrying down of any molybdenum that may be held by  $\text{WO}_3$ , if any tungsten is present.

(2) The addition of tartaric acid prior to the passing of  $\text{H}_2\text{S}$  is for the purpose of obtaining  $\text{MoS}_3$  uncontaminated by either tungsten or vanadium. The acids of these metals form complex compounds with tartaric acid and they are not precipitated by  $\text{H}_2\text{S}$ .

(3) A small amount of molybdenum is reduced to lower stages of valency on passing  $\text{H}_2\text{S}$  and the reduced compounds are not precipitated by  $\text{H}_2\text{S}$ . The filtrate from the bulk of  $\text{MoS}_3$  will contain those reduced compounds. They are therefore dealt with by the colorimetric method.

(4) As ferromolybdenum contains a small amount, about 0.2% of copper, this must be eliminated before putting the molybdic acid solution through the reductor.

(5) The solution of the sulphide with the filter paper in  $\text{HNO}_3$ , may give rise to certain organic compounds which are reduced by passage through the Jones reductor. The elimination of these as oxidised products is effected by  $\text{KMnO}_4$ .

## EXPERIMENT 78 F.

### Ferro-Tungsten.

#### Determination of Tungsten.

##### Principle :—

The alloy is opened out with  $\text{HF}$  and  $\text{HNO}_3$  and fumed with  $\text{H}_2\text{SO}_4$ . The impure tungstic acid is filtered off, ignited and weighed. The ignited residue is fused with  $\text{Na}_2\text{CO}_3$ , extracted with water, filtered and the residue is ignited and weighed. This weight is subtracted from the weight of impure tungstic acid and, from the weight obtained, the weight of tungsten is calculated.

##### Procedure :—

Weigh 1 gm. sample of the material passing through a 100 mesh sieve into a 60-75 ml. capacity platinum dish, add 5 ml. of  $\text{HF}$  and heat. Add 30 ml. of conc  $\text{HNO}_3$  drop by drop from a dropping bottle until the alloy is in solution. Add 15 ml. of 1:1 dil.  $\text{H}_2\text{SO}_4$  and heat until dense fumes of  $\text{SO}_3$  are evolved. To avoid spattering, the heating must be done on a sand bath. Cool and transfer the contents of the dish to a 400 ml. beaker with the cautious addition of water. Rinse the dish with water 3 or 4 times each time using 10 ml. of water. Transfer the rinsings to the beaker. Dissolve the yellow residue adhering to the dish in dil.  $\text{NH}_4\text{OH}$  ( 1:1 ) and add the solution to the beaker. Repeat solution in ammonia and finally rinse the dish with water. Bring the volume of solution



to about 150 ml. by dilution with water. Add 10 ml. of conc. HCl and boil for 5 minutes. Remove the beaker from the source of heat, and dilute to about 350 ml. with water. Add 10 ml. of dil. HCl ( 1:1 ) containing 1.25 gm. of cinchonine. Introduce a little paper pulp. Heat to about 75° C and let stand for 3-4 hours or until the supernatant liquid is clear. Filter. Wash with a solution of cinchonine hydrochloride ( 4 gms. of cinchonine in 30 ml. of dil. HCl ( 1:1 ) and the solution diluted to 1000 ml. with water ) and finally with dil. HCl ( 1:99 ). Transfer the filter-paper with the residue to a platinum crucible, gently ignite until the carbon is consumed and then in an electric muffle furnace kept at a temp. not exceeding 750° C. Cool and weigh.

Purify the impure tungstic acid contaminated with a little ferric oxide, manganese oxide and/or chromium oxide by fusion with  $\text{Na}_2\text{CO}_3$  ( 5-6 gms ) in the same platinum crucible. Extract with hot water and a little alcohol and filter. Wash filter paper with hot water. Ignite, cool and weigh. Subtract the weight of the residue from the original weight of  $\text{WO}_3$ +impurity. Calculate % of tungsten from the weight of the pure  $\text{WO}_3$ .

NOTES :—

(1) If molybdenum is present in the alloy, this will be present in the filtrate from the  $\text{Na}_2\text{CO}_3$  fusion. This may be determined colorimetrically as described under the heading 'Ferromolybdenum' above.

(2) A blank should be run for silica in  $\text{Na}_2\text{CO}_3$  and the weight of  $\text{SiO}_2$  subtracted from the weight of  $\text{Fe}_2\text{O}_3$  etc. impurity in the residue resulting from the fusion of  $\text{WO}_3$  and the extraction and filtration of the same.

(3) See Expt. 31, p 198 re use of cinchonine hydrochloride.

## Determination of Phosphorus

### Ferro-Phosphorus

#### EXPERIMENT 78 G.

##### Principle :—

See Expt. 78 C Notes. The alloy is opened out by heating it in a platinum dish with Rothe mixture. The sintered mass is then dissolved in water, evaporated to dryness with HCl. The residue is extracted with dil. HCl, the silica filtered off and the filtrate made to a definite volume. From an aliquot part of the filtrate, the phosphorus is precipitated as ammonium phospho molybdate. This is filtered off and the precipitate dissolved in standard NaOH solution. See Expt. 16.

##### Procedure :—

Proceed as in Note 1, Expt. 78 C. Carry out the evaporation to dryness, baking, filtering off etc. operations, twice. Make up the combined filtrates to 500 ml. in a graduated flask. Mix thoroughly. Pipette off 20 ml. into a conical flask. Evaporate to low bulk twice with 20 ml. conc.  $\text{HNO}_3$ . Oxidise with a solution of  $\text{KMnO}_4$  (4%) and destroy the excess with  $\text{KNO}_3$  solution. Boil off the nitrous fumes. Cool to  $70^\circ\text{C}$ . Add 50 ml. of  $(\text{NH}_4)_2\text{MoO}_4$  solution. Let stand, filter, wash and complete as in Expt. 16.

#### EXPERIMENT 78—H.

### Analysis of Calcium Silicide.

##### Outline of Procedure :—

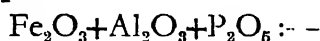
The crushed alloy is opened out by a fusion attack with fusion mixture and a little  $\text{KNO}_3$  in a platinum crucible. The solidified melt is extracted with water, evaporated to dryness with

HCl and baked. The baked mass is redissolved in HCl and filtered. The filtrate is evaporated to dryness a second time and baked. The baked mass is redissolved in HCl and the solution filtered on a separate filter-paper. The two residues are combined, ignited in a platinum crucible, cooled and weighed. The residue is then hydrofluorised, ignited, cooled and weighed. From the loss in weight, the % of silicon is calculated. Calcium is determined from the filtrate as follows :—

A basic acetate separation yields  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{P}_2\text{O}_5$  as residues. The filtrate from the above is treated with ammonium oxalate for the separation of  $\text{CaC}_2\text{O}_4$  which is then dealt with as in Expt. 11.

### Silicon :—

**Procedure** :—Fuse 0.5 gm sample with 8 to 10 gms. of fusion mixture and 0.5 gm.  $\text{KNO}_3$  in a platinum crucible and proceed with the melt for silicon as in Expt. 78-C



Proceed with the filtrate from  $\text{SiO}_2$  as in Expt. 21.

Ignite the residue from the basic acetate separation and weigh. Determine Fe and P as in Expts. 10 and 14 respectively. Convert into oxides and subtract from the total. Difference is  $\text{Al}_2\text{O}_3$ .

**CaO** :—Proceed with the filtrate from the above as in Expt 11.

**Note.** This alloy is employed as an addition to ladle charges containing molten iron from cupola and to steel from the open hearth furnace. In the former case finely divided and distributed graphite is formed and castings made from such metal are known as meehanite castings.

## EXPERIMENT 78 J.

**Qualitative Tests for Alloying Elements in Steels.****a. Detection of Chromium :—**

The qualitative test is based on the formation of a violet coloured solution when a solution of diphenylcarbazide in a mixture of glacial acetic acid and alcohol is added to an alkali chromate solution free from salts of Cu, Fe, Ni and Co and acidified with dil.  $\text{H}_2\text{SO}_4$ .

**Reagent :—**

Dissolve 0.2 gm. of diphenyl carbazide in a mixture of 10 ml. glacial acetic acid and 90 ml. of ethyl alcohol.

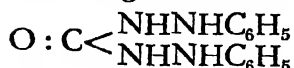
**Procedure :—**

Dissolve 0.1 to 0.5 gm. of the steel sample to be tested in a boiling tube of about 70-100 ml. capacity in 10 ml. of dil  $\text{H}_2\text{SO}_4$  (1 : 1). Add a 4% solution of  $\text{KMnO}_4$  in drops until a pink colour persists. Boil for 2-3 minutes. Filter off the  $\text{MnO}_2$  precipitate through asbestos pad. The filtrate should be free from the pink colour due to  $\text{KMnO}_4$ . If a pink colour shows, repeat boiling with the addition of a few mgms. of  $\text{MnSO}_4$  and filter. To the filtrate add  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$ , filter off  $\text{Fe}(\text{OH})_3$ . Acidify filtrate with dil.  $\text{H}_2\text{SO}_4$  (1 : 4). Now add a few drops of the reagent. A violet colour shows the presence of chromium.

**NOTES :—**

(1) Alloying elements like nickel, cobalt and copper also give colour reactions with the reagent. They must be removed before applying the test. This is readily done by adding  $\text{NaOH}$  to the chromate solution, boiling and filtering off the ppt. The filtrate is acidified with dil.  $\text{H}_2\text{SO}_4$  and the test is then applied.

(2) The reagent has the formula—



(3) Alternatively, test as follows for the presence of chromium :—Dissolve 0.1 to 0.2 gm of the steel to be tested in 5 ml. of dil.  $\text{H}_2\text{SO}_4$  (1 : 3) in a test tube by heating for half of an hour in a boiling water bath. Similarly dissolve 0.1 to 0.2 gm of a sample of plain carbon steel in exactly the same way. Hold the two test tubes against a white background. A green colouration due to the formation of  $\text{Cr}_2(\text{SO}_4)_3$  will appear in the tube containing the steel to be tested, in case Cr is present. The green colour also forms if nickel is present but this colour is much less intense.

#### b. Detection of Nickel:—

Dissolve 0.1 to 0.2 gm. of the steel sample in 5 ml. of dil  $\text{H}_2\text{SO}_4$  (1 : 3) in a test tube by heating in a water bath. Add a few drops of dil  $\text{HNO}_3$  (1:3) to oxidise the ferrous iron. Dilute to about 15 ml. with water. Add 0.5 gm. of tartaric acid and shake until dissolved. Add  $\text{NH}_4\text{OH}$  (1:3) until slightly ammoniacal. Add a few drops of a 1% solution of dimethyl glyoxime in ethyl alcohol. A bright red coloured precipitate or only a red colour shows the presence of nickel. For the composition of the ppte. see Expt. 28.

#### c. Detection of Molybdenum.

##### Procedure :—

Dissolve 0.2 gm. of the steel sample in 10 ml. of dil.  $\text{HCl}$  (1:1) in a boiling tube of 100 ml. capacity. Add 0.5 gm. of  $\text{KClO}_3$ . Boil to expel the free chlorine after dilution with water to about 20 ml. Add to distinct alkalinity a 10%  $\text{NaOH}$  solution, boil and filter. Acidify the filtrate with dil.  $\text{H}_2\text{SO}_4$  (1:4) and add a few drops of a 2% solution in ethyl alcohol of the reagent

*a*-benzoin oxime. A white turbidity shows the presence of molybdenum.

The reagent has the formula—



An alternative test for molybdenum in steel consists in the formation of a blood-red colour when a solution of KCNS is added to a solution of an alkali molybdate acidified with dil.  $\text{H}_2\text{SO}_4$  and treated with  $\text{SnCl}_2$  solution. The blood-red coloured compound has the formula  $\text{Mo}(\text{OH})_3(\text{CNS})_3$ . See Expt. 34.

#### d. Detection of Copper

Dissolve about 0.1 gm. of the sample in 5 ml. of dil.  $\text{H}_2\text{SO}_4$  ( 1:3 ) in a test tube. Transfer the solution to a small size beaker. Add 1 gm tartaric acid and shake until dissolved. Add  $\text{NH}_4\text{OH}$  ( 1:1 ) until ammoniacal. Place a drop of the reagent *a*-benzoinoxime dissolved in alcohol ( a 2% solution ) on a strip of filter-paper. Dry the same. Add a drop of the solution of steel and dry. A green colour shows the presence of copper. The reagent is known as 'cupron'.

#### e. Detection of Cobalt

Reagent:—

A 1% Solution of the substance *a*-nitroso— $\beta$  naphthol in glacial acetic acid.

Procedure :—

Dissolve about 0.1 gm. of the steel sample in 5 ml. of dil.  $\text{HCl}$  ( 1:1 ) in a test-tube with the aid of heat. A green coloured solution when hot suggests the presence of cobalt. The green colour disappears on cooling the solution to room temperature. Confirm by oxidising with a few drops of conc.  $\text{HNO}_3$  and boiling until excess of the acid and the oxides of nitrogen are expelled. To the cold solution add  $\text{NH}_4\text{OH}$  until ammoniacal and dil.  $\text{HCl}$  ( 1:1 ) until acid and then add a few drops of

the reagent. A red ppte. or colour shows the presence of cobalt. Alternatively, add to the above solution of steel not containing  $\text{H}_2\text{SO}_4$ , 2 gms. of ammonium acetate and 1 ml. of an alcoholic solution containing per 100 ml. of it 0.5 gm. of benzidine and 0.25 gm. of dimethyl glyoxime. An intense orange colour is produced.

The test may also be applied to the filtrate from nickel which has been tested for by the addition of an alcoholic solution of dimethylglyoxime, provided no sulphates are present. This will be the case if no sulphuric acid is employed for dissolving the steel.

**f. Detection of Tungsten :—**

Dissolve about 0.1 to 0.2 gm. of the steel sample in 5 ml. of dil.  $\text{H}_2\text{SO}_4$  ( 1:3 ) in a boiling tube. When almost dissolved, add conc.  $\text{HNO}_3$  from a dropping bottle in drops. Heat after the addition of a few drops. Particles of a yellow colour indicate the presence of tungsten. The ppte. is due to the formation of tungstic acid of the formula  $\text{WO}_3$ .

**g. Detection of Vanadium :—**

The test is based on the formation of a reddish-brown colour when  $\text{H}_2\text{O}_2$  is added to a solution of vanadic acid. The vanadic acid is itself coloured yellow or orange depending upon its freshness and concentration. In large dilutions, the yellow or the orange colour may not be pronounced.

**Procedure:—**

Dissolve about 0.1 to 0.2 gm. of the steel sample in 5 to 10 ml. of dil.  $\text{HNO}_3$  ( 1:1 ) in a boiling tube by heating for a few minutes over a Bunsen burner. Add dil.  $\text{H}_2\text{SO}_4$  ( 1:1 ) and heat to expel  $\text{HNO}_3$ . Add normal  $\text{KMnO}_4$  solution in drops until a pink colour persists. Boil until the pink colour is destroyed and the superna-

tant liquid does not show any pink colour on standing. Filter off  $\text{MnO}_2$  ppte. and add  $\text{H}_2\text{O}_2$  to the cooled filtrate. An orange red colour shows the presence of vanadium. Pervanadic acid of the formula  $\text{HVO}_4$  is formed and has the orange red colour.

NOTE :—

Titanium modifies the colour but it is eliminated by boiling with  $\text{NaOH}$  the solution of the steel sample and filtering off the sodium meta titanate and making the addition of  $\text{H}_2\text{O}_2$  to the cooled filtrate. acid with dil.  $\text{H}_2\text{SO}_4$

#### **h. Detection of Aluminium :—**

The test is based on the formation of a red colour or precipitate when the solution to be tested is treated with a solution of the ammonium salt of aurine—tricarboxylic acid.

**Reagent :—**

Dissolve 0.1 gm. of the reagent in 100 ml. of water.

**Procedure :—**

Dissolve about 0.5 gm. of the sample of steel to be tested in 20 ml. dil.  $\text{H}_2\text{SO}_4$  (1:4) in a boiling tube. Oxidise the iron by  $\text{HNO}_3$ . Add  $\text{NaOH}$  solution until strongly alkaline, boil and filter. Acidify 5 ml. of the filtrate with dil.  $\text{HCl}$  (1:2) until the medium is about normal with respect to  $\text{HCl}$ . Mix with 5 ml. of 3 N ammonium acetate solution and 5 ml. of the reagent. Add ammonium hydroxide until slightly alkaline, then add  $(\text{NH}_4)_2\text{CO}_3$  solution. A red colour shows aluminium. That due to chromium is destroyed by ammonia. The reagent is known as 'aluminon' and has the formula  $(\text{C}_6\text{H}_3\text{OHCOONH}_4)_3 : \text{C} : \text{C}_6\text{H}_3 (\text{COONH}_4) : \text{O}$ . Nitriding steels contain aluminium and molybdenum.



## EXPERIMENT 78 K.

**Alloying Elements in Aluminium Alloys.****Detection of Nickel :—**

The test is based on the formation of a red colour or precipitate when a drop of an alcoholic solution of dimethyl glyoxime is placed on the surface of the alloy which has been treated successively with drops of a solution of NaOH and of  $\text{HNO}_3$ . The sodium hydroxide solution dissolves the aluminium but leaves the nickel unattacked. This is dissolved by the addition of nitric acid. The solution of nickel forms the red complex with the reagent. For the formula, see Expt. 28.

**Reagents :—**

1. A 20% solution of caustic soda.
2. Dilute  $\text{HNO}_3$  1:1.
3. 1% alcoholic solution of dimethyl glyoxime.

**Procedure :—**

Allow one drop of Reagent No. 1 to act on the surface of the alloy piece for 2-3 minutes. Add 2 drops of dil.  $\text{HNO}_3$  ( 1:1 ). Mix with a glass rod and add 2 drops of Reagent No. 3. A rose-coloured precipitate shows the presence of nickel.

**Detection of Copper :—**

As in the case of copper in steel, the test is based on the formation of a green colour when an alcoholic solution of  $\alpha$ -benzoinoxime is added to a copper salt.

**Reagents :—**

1. 20% NaOH solution.
2. 20 gms of ammonium tartrate dissolved in 100 ml. of water and the solution made ammoniacal with 1:1  $\text{NH}_4\text{OH}$ .
3. 1 gm. of  $\alpha$ -benzoin oxime in 100 ml. of rectified spirit.

**Procedure :—**

Apply one drop of the reagent no. 1 to the surface of the alloy. Let it act for 2-3 minutes. Absorb the excess of the reagent in a strip of filter-paper. Add 3 drops of the reagent no. 2 and then 1-2 drops of the reagent no. 3. A green colouration shows the presence of copper.

**Detection of Manganese :—**

The test is based on the formation of a pink colour due to the production of permanganic acid when a few particles of sodium bismuthate are sprinkled over the surface of an alloy which has been successively treated with drops of a solution of NaOH and of  $\text{HNO}_3$ .

**Reagent :—**

1. A 20% NaOH solution
2. Dil.  $\text{HNO}_3$  ( 1:1)
3. Sodium bismuthate.

**Procedure :—**

Apply 1 drop of reagent no. 1. to the surface of the alloy. Allow the reaction to proceed for a minute or two. Add 2 drops of reagent no. 2., mix well with a glass rod and sprinkle on a few milligrams of sodium bismuthate. A purple colour gradually developing shows the presence of manganese.

**EXPERIMENT 78 L.****Impurities in Copper.****Bismuth :—**

The test is based on the formation of an orange-red precipitate or colour, when a strip of filter paper is moistened with a drop of the test solution and then treated with a drop of an aqueous solution containing cinchonine and potassium iodide.

**Reagent :—**

Dissolve 1 gm. of cinchonine in 100 ml. of warm water acidified with nitric acid. Cool. Add 2 gms. of KI.

**Procedure :—**

Dissolve about 0.2 gm. of the sample in 5 ml. of dil.  $\text{HNO}_3$  ( 1:1 ). Expel the excess of  $\text{HNO}_3$  by fuming with dil.  $\text{H}_2\text{SO}_4$ . Place a drop of the reagent on a strip of filter-paper. Then add a drop of the solution to be tested. An orange coloured ring shows the presence of bismuth, yellow ring, if any, being due to lead and a brown ring due to cuprous iodide and free iodine.

**Antimony :—**

The test is based on the formation of a characteristic crystalline precipitate, when seen with a lens, forming when a solution of the metal in the pentavalent condition is tested on a glass slide with a small quantity of pyrogallol.

**Procedure :—**

Dissolve about 0.2 gm. of the metal in 10 ml. of dil.  $\text{HNO}_3$  ( 1:1 ) in a boiling tube. Dilute with water to about 20 ml. Place one drop of this on a glass slide. Sprinkle a small quantity, about 5 mgms., of pyrogallol, stir with a rod until dissolved. A characteristic shaped crystalline precipitate forms in a few minutes.

**EXPERIMENT 78 M****Tin in Lead-Antimony Alloys.****Tin :—**

The test is based on the formation of a violet-coloured compound formed by solutions containing tin in the stannous condition when treated with an aqueous solution of cacotheline.

**Reagent :—**

Make a saturated solution in water of the reagent cacotheline.

**Procedure :—**

Dissolve about 0.2 gm. of the alloy contained in a 100 ml. Kjeldahl flask in 10 ml. of conc. HCl to which a pinch of  $\text{KClO}_3$  has been added. Heat to help solution. Dilute with water to about 50 ml, and boil down to about 20 ml. to expel chlorine. Add a strip of aluminium to the solution along with a few ml. of conc. HCl. Place a drop of the reagent on a strip of filter paper. Add one drop of the filtered and cold solution to the strip at the point where it has been moistened. A violet spot on the background of yellow shows the presence of tin. The test is not available in the presence of the following—Ag, Cr, Cu, Fe + + +, Hg, Co, Ni, Mo, V, and Sb + + +.

Cacotheline has the formula  $\text{C}_{31} \text{H}_{21} \text{O}_7 \text{N}_8$ .

**EXPERIMENT 78 N****Beryllium in Copper Alloys.****Principle :—**

The test is based on the formation of a blue colour when a solution of quinalizarin in sodium hydroxide is added to a solution of beryllium salt free from the salts of Mg, Co, and Cu.

**Reagent :—**

The reagent should be freshly made each time it is required by dissolving 40 mgms. of quinalizarin in 100 ml. of a 1% solution of NaOH in water.

**Procedure : —**

Add a few drops of the reagent to 10 ml. of the solution of 0.1 gm. of alloy in 3 ml. of 1:3  $\text{HNO}_3$ . Add 1% NaOH solution until distinctly alkaline. A blue

colour shows the presence of beryllium. The test is made more certain by running a parallel test in a second test-tube using the same volumes of the reagent and of NaOH solution. If beryllium is present, the test will yield a more distinctly blue colour than the parallel blank test.

Interference due to magnesium salt is destroyed by the cautious addition of bromine water. Too liberal an addition of bromine water will tend to destroy the blue colour due to beryllium. That due to the presence of one or all of the following, namely, salts of Ni, Co, and Cu, is eliminated by the addition of excess of KCN solution. That due to aluminium is eliminated by a liberal addition of NaOH solution. The alloys containing beryllium are readily brought into solution in  $\text{HNO}_3$ . The cold solution on treatment with excess of KCN solution yields the copper in the form of a complex compound in solution. Place one drop of this solution on a strip of filter paper and then a drop of the reagent. A blue colour will be formed, which is distinct from the colour due to the reagent.

Minerals should be opened out by fusion with  $\text{Na}_2\text{CO}_3$  in a platinum crucible. The melt should be extracted with water, treated with dil. HCl (1:1), filtered and then the above test applied to the filtrate.

The reagent is also known as 1:2:5.8 tetrahydroxy anthraquinone. The formula is  $(\text{OH})_2\text{C}_6\text{H}_2(\text{CO})_2\text{C}_6\text{H}_4$ .

# **CHAPTER X.**

## **EXAMINATION OF SOLD, LIQUID AND GASEOUS FUELS AND ANALYSIS OF FLUE GAS AND LUBRICATING OILS.**

### **EXPERIMENT 79.**

#### **Proximate Analysis of Coal :—**

The Proximate Analysis of Coal includes the following determinations :—Moisture, Volatile matter, Ash and Fixed Carbon. The last three are made on the moisture-free sample. The first three are obtained by direct experiment and the last, namely, fixed carbon, is obtained by difference. Unlike the determinations made on samples of iron, steel, ferrous and nonferrous alloys, those made on coal are subject to great variations on account of its inherently complex nature and the non-uniformity of the apparatus used and the procedure adopted in different laboratories. In recent years great attention has been paid to these aspects by the Fuel Research Board of England and by the American Society for Testing Materials of the U. S. A. . The methods described here are those evolved by these two bodies. Procedures are included which may be adopted in Laboratories lacking the standard equipment.

For the Proximate Analysis, the powder passing through a 60 mesh sieve ( specified by the Institution of Mining and Metallurgy ) is used.

#### **Determination of Moisture :—**

Owing to the tendency of coal to oxidise in an ordinary air-oven, when the moisture in it is expelled .

by heating to 105 to 110°C., the apparatus shown in Fig 23, which makes it possible to employ dry  $N_2$  or  $CO_2$ , is used. The chamber in which the sample is heated is surrounded by a glycerine-water mixture of such composition that it boils at 105 to 110°C. One part by volume of glycerine mixed with six parts by volume of water boils within this range. The spherical condenser C serves to maintain the composition of the mixture constant. A coil of copper tube surrounds the

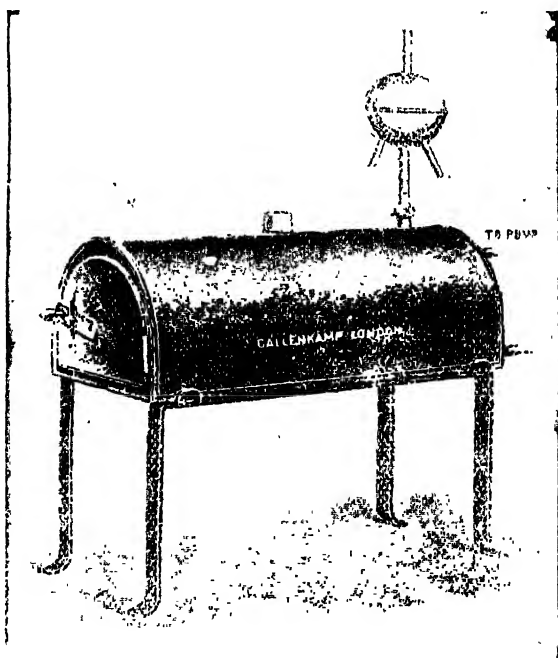


Fig. 23.

chamber and is immersed in the bath of glycerine-water mixture. The end A of the coil projecting at the back of the chamber is connected through a wash-bottle

containing about  $\frac{1}{2}$  to 1 inch layer of conc. sulphuric acid. The other end of the coil terminates at the base of the chamber at the front. The tube B at the back is connected to the Laboratory Bunsen's filter-pump. During a run, the water-tap is turned on, a stream of air is drawn through the conc.  $\text{H}_2\text{SO}_4$ , dry air enters the chamber and takes up the moisture in the coal and is drawn out through B. Instead of dry air, either dry nitrogen or dry carbon dioxide may be circulated through the chamber, after drying it by passing through the wash bottle containing conc.  $\text{H}_2\text{SO}_4$ . The atmosphere of  $\text{CO}_2$  or  $\text{N}_2$ , being non-oxidising, is best. The rate of passing the dry gas should be such that the atmosphere of the chamber is renewed 3 to 4 times every hour.

Containers for the sample of coal are silica dishes about  $1\frac{3}{4}$  inch in diameter and  $\frac{3}{8}$  inch deep. The weight of the sample should be related to the diameter such that 0.3 gm of the coal is exposed per sq. cm. of area. The dishes are provided with tightly fitting aluminium lids which are stamped with the numbers 1,2,3, etc. These serve to prevent confusion of samples when a number of them is handled at the same time. A copper sheet tray with holes for the reception of the dishes forms part of the equipment. The insertion and withdrawal of a number of samples into the drying chamber is facilitated by this.

Weigh 1-2 gms. of the sample into the dish and cover it when making the weighing. Uncover the dish when making a moisture determination. Heat for one hour. Withdraw from the heating chamber. Cover with the lid, allow to cool in a desiccator charged with concentrated sulphuric acid and weigh with the lid. The loss of weight represents the moisture.



**Determination of Volatile Matter :—**

Introduce into a weighed platinum crucible with tightly fitting lid 1 gm. of the sample of moisture-free coal. The lid has a hole 1 mm. diameter in the middle to help the escape of volatile matter. Support the crucible on a platinum wire triangle and heat for seven minutes in a Davies crucible furnace, Fig. 24. The flame should have a height of about 20 cms. and the bottom of the crucible should be some 8 cms. above the top of the burner.

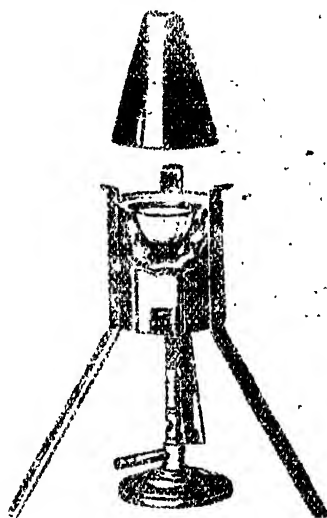


Fig. 24.

Cool in a desiccator and weigh. The difference in weight represents the amount of volatile matter. The determination may be carried out by heating in a muffle furnace. The crucible should in this case be supported

on a pipe clay triangle bent suitably so that the bottom of the crucible does not touch the floor of the muffle.

This determination does not lead to concordant results when the experimenters do not observe the same set of conditions in performing the test. These are arbitrarily fixed and vary in different countries. The temperature reached must be  $925^{\circ} \pm 25^{\circ}\text{C}$ , according to the Fuel Research Board, England. This condition is fulfilled if a few crystals of potassium chromate placed in an empty crucible show signs of melting on heating the covered crucible in the furnace.

Duplicate results obtained by the same operator, expressed as percentages on the sample, should not differ by more than 0.5.

The 'volatile matter' consists of many carbon compounds and free hydrogen.  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$  and  $\text{H}_2$  form the major constituents and  $\text{C}_6\text{H}_6$  the minor constituent of the gas-mixture. The test does not however give any insight into the nature of the compounds present or their amount.

### Determination of Ash

Heat in a muffle furnace the silica dish containing the sample of coal which has been freed from moisture until all the carbon particles are burnt. This takes about  $1\frac{1}{2}$  hours. The dish must be placed at the mouth of the muffle for about 10 minutes and then gradually pushed into the hottest part. Suddenly introducing into the hottest part will lead to mechanical loss.

In the absence of a muffle furnace proceed as follows :—

Cut out a hole in a piece of asbestos board sufficient in size to expose the bottom of the dish to the full effect of the flame of a Bunsen burner. Raise the heat gradually. Stir from time to time with the help of a stout platinum wire. Heat until all the carbonaceous matter is burnt out ( 2 hours ). Cool and weigh. The use of a platinum dish will very much shorten the duration of the experiment.

To test whether all the carbon particles have been burnt, proceed as follows :—

Moisten the ash with a few drops of alcohol : if black specks appear, burn off the alcohol carefully over a low flame and then ignite in the muffle.

### **Calculation of Fixed Carbon.**

Deduct from 100, the sum of the percentages of 'Volatile Matter' and 'Ash'.

### **Determination of Sulphur in Coal.**

#### **Principle :—**

Sulphur existing in coal as sulphide and sulphate or iron, calcium sulphate and complex organic sulphides, is converted into sodium sulphide or sulphite by heating to  $900^{\circ}\text{C}$  with  $\text{Na}_2\text{CO}_3$ . The product is then oxidised by bromine to sulphate of sodium. This is precipitated by means of  $\text{BaCl}_2$ .

#### **Procedure :—**

Weigh 1 gm. of the sample into a platinum crucible. Add to it 3 gms. of Eschka mixture. This mixture consists of 1 part of anhydrous sodium carbonate and 2 parts of magnesium oxide. Mix the two well with a short glass rod or by means of a spatula. Brush the rod or the spatula. Cover with 1 gm. more of the mixture. Place in a cold muffle furnace and make the

burners on. Heat until all the carbon is burnt. This takes about 1 hour calculating from the time the muffle is dull red. If no muffle furnace is available, cut out a hole in a piece of asbestos board which is big enough to allow the lower  $\frac{3}{4}$  of the crucible to project below. Support the asbestos board on a tripod and raise one of its legs slightly. This arrangement prevents the absorption of the gases  $\text{SO}_2$ ,  $\text{SO}_3$  resulting from the combustion of laboratory gas supply, from being taken up by the contents of the crucible. Heat over a Bunsen burner, gradually raising flame to full height. Stir the mass from time to time with a stout platinum wire, or a nickel-plated spoke of a cycle. When no more black particles are to be seen, remove the burner. Allow the crucible to cool. Transfer the contents to a beaker of 200 ml. capacity. Add 1 ml. of bromine-water and 100 ml. of distilled water. Boil, filter and wash the residue by decantation 3 or 4 times, collecting the filtrate in a 500 ml. beaker. Acidify the filtrate with dil.  $\text{HCl}$  (1 : 1). When the bromine colour is removed by boiling the filtrate, add 10 ml. of 10%  $\text{BaCl}_2$ , continue boiling 2 minutes longer. Allow to stand for 12 hours. Filter off the precipitate of  $\text{BaSO}_4$ . Wash until free from chloride, ignite and weigh. From the weight of  $\text{BaSO}_4$  calculate the percentage of S.

NOTES :—

(1) Sulphur-di-oxide is among the products of combustion of coal. The latter is taken up by  $\text{Na}_2\text{CO}_3$  yielding  $\text{Na}_2\text{SO}_3$ . The temperature at which the oxidation of carbon and other combustible matters takes place fairly rapidly is about  $900^\circ\text{--}950^\circ\text{C}$ . At this temperature  $\text{Na}_2\text{CO}_3$  will be in a liquid condition, its melting point being  $850^\circ\text{C}$ . In the absence of  $\text{MgO}$  the molten liquid will enclose particles of coal which will

not render up their sulphur content as  $\text{SO}_2$  and thus low results will be obtained. By admixture with  $\text{MgO}$  which is a very good basic refractory, the mass of coal is kept open to oxidation and all the sulphur is burnt to  $\text{SO}_3$ . Lime may be substituted for  $\text{MgO}$  in the preparation of the 'Eschka mixture'. The procedure in this case is exactly the same as above.

(2) In the Laboratories of Europe and America, coal-gas is commonly used. This contains a fair percentage of sulphur vitiating the result of an assay like the one on hand. A 'blank run' is made with the reagents used in the actual run, the crucible of the blank run being heated for the same length of time as that of the assay. The weight of  $\text{BaSO}_4$  obtained in the 'blank run' is subtracted from that obtained for the assay and the calculation is then made for the sulphur in the assay. If the reagents are pure, no vitiation of results follows the use of oil-gas made from a low grade kerosene oil, which gas forms the bulk of the supply to Laboratories located in centres far removed from the great cities, if a blank run is omitted. Nevertheless, it is always advisable to make a blank run for sulphur along with the assay of Coal.

(3) In the absence of a platinum crucible, a nickel or a porcelain crucible may be used. The latter becomes unserviceable for any other purpose but for sulphur determinations, when once it has been used.

(4) The method is also available for the determination of sulphur in coke ; only in this case heating with the 'Eschka mixture' for a longer time is necessary.

(5) When the calorific value of the sample of coal is determined using the 'Bomb Calorimeter', sulphur may be determined from the Bomb washings.

## EXPERIMENT 80.

**Determination of the Calorific Value of Coal  
( The Lewis Thompson Calorimeter. )**

Fig. 25 shows the separate parts of the calorimeter.

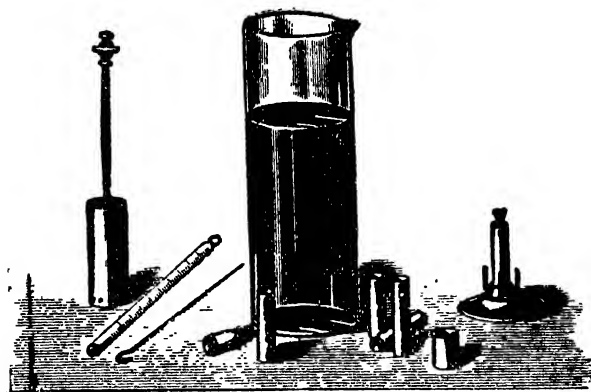


Fig 25.

A is a large glass cylinder holding 2000 ml. of water when filled to the mark. B is a copper cylinder open below and has 8 holes each about  $\frac{1}{8}$  inch in diameter, equally spaced all round the wall and about  $\frac{1}{2}$  inch from the bottom. It is 2 inches in diameter and about 9 inches high. It is closed above by the copper pipe and tap through which the products of combustion are allowed to escape, when the combustion of coal is at an end. The equally spaced holes at the bottom of B permit the escape of the products of combustion during a run. C is a small copper cylinder 4 inches high,  $\frac{1}{2}$  inch in diameter and closed at the bottom in which the combustion of the fuel takes place. D is the holder for the same. E is a thermometer graduated in tenths of a degree and reading to  $45^{\circ}\text{C}$ . The procedure is as follows :—2 gms of the finely powdered and dried sample of coal ( through 60 mesh sieve, I. M. M. ) are

weighed out on a sheet of glazed paper and intimately mixed with 22 gms of 'oxygen mixture' which is made as follows :—3 parts of  $\text{KClO}_3$  and one part of  $\text{KNO}_3$  are mixed and dried. The mixing of the coal sample with the 'oxygen mixture' must be very intimate. When this is the case, the mixture will have a grey colour. This mixture is transferred to C in small quantities at a time and is pressed after each transfer with the flattened end of a wooden rod. When all of it has been transferred, C is placed in the holder D, a few strands of fuse are embedded in the top of the mixture, the projecting free ends are lighted with a match-stick and after quickly covering with the copper cylinder B, the tap at the top being closed, the whole is placed in the vessel A containing 2000 gms. of water, the temp. of which has been carefully noted. When no more gas bubbles issue from the holes at the side of B, open the tap at the top of B to allow the water to have access to C. Thoroughly mix the water in A by moving B up and down in it. Note the final temperature. If  $t$  is the rise of temperature in degrees C., 2000 gms., the weight of water used, 2 gms. the weight of coal, 'c' the calorific value is given by the equation  $c = (2000 + w) t/2$  where 'w' is the water equivalent of the calorimeter, c being expressed in gm. calories. The value of 'w' is best ascertained by using a standard sample of fuel of known calorific value and by using 'w' as the unknown in the above equation in place of c, the value of which is inserted.

The following improvements of the original apparatus have been suggested by J Kershaw and they are claimed to give more accurate results :—

Weight of water used is 3000 gms. A thin Jena glass beaker replaces the thick vessel shown in Fig. 25. This change lessens the rise in temp. thereby diminishing radiation losses.

Radiation losses are further minimised by the use of a tin cylindrical shield which surrounds the beaker and provides a non-conducting air jacket between the water and the outside air.

A copper gauze ring is provided to fit on to the copper cylinder B and nearly touches the beaker at all points. This breaks up the bubbles that pass through the water on making a test and causes the waste gases to be better cooled.

The oxygen mixture is dried, before use, for 1 hour at  $110^{\circ}\text{C}$ . The amount to be employed is obtained from  $W = (100 - a) / 4$  where  $W$  is the weight of oxygen mixture required for 2 gms. of coal and ' $a$ ' the percentage of ash in the sample of coal to be tested.

Tight packing and loose packing are alike objectionable. Ignition fuse is made of 4 strands of lamp wick dipped in concentrated  $\text{KNO}_3$  solution and dried.

Water equivalent is obtained by putting through the above operations 2 gms. of a sample of coal whose heating value is exactly known.

Neither the original nor the modified apparatus is suitable for the determination of the heating value of non-coking coals, anthracite, etc. These coals ignite with difficulty and are incompletely burnt. A sample of coal from the colliery at Umaria, Central Provinces, did not ignite at all. The heating value of such coals can be determined only with the 'bomb' calorimeter.

Even with coals that readily ignite, the heating values obtained with the Lewis Thompson calorimeter are 10% lower than the values obtained on the same sample with the 'bomb' calorimeter. It is therefore usual to add 10% to the value obtained with the Thompson calorimeter to make it approximate to the value that would be obtained with the bomb calorimeter.



2 gms. of a sample of coal gave with the Lewis Thompson calorimeter  $5.5^{\circ}\text{C.}$  rise, 2000 gms. of water were used in the calorimeter-jar. The corrected heating

$$\text{value of the Coal} = 1000 \times 5.5 + \frac{1000 \times 5.5}{10}$$

$$= 5500 + 550 \text{ gm. cal.}$$

$$= 6050 \text{ gm. cal.}$$

## EXPERIMENT 81.

### The Emerson Bomb Calorimeter..

Unlike the Lewis Thompson calorimeter, this has a wider range of usefulness in that it can be used with all classes of solid and liquid fuels. The essential feature of the determination of the heating value with this instrument consists in burning the fuel in an atmosphere of oxygen confined at a pressure of 300 lbs. per sq. inch in a 'bomb' or steel shell made to withstand a pressure of 1000 atmospheres. The ignition of the fuel, coal or oil, is effected by means of a wire raised to a glow by a current of electricity. The stirring of the water is done by means of an electric motor. Radiation losses are reduced to a minimum by resting the calorimeter on cork support inside a double walled cylindrical vessel, the annular space between the two walls being filled with water.

### Description of the bomb and procedure :

The bomb or shell (Fig. 26) is made in two halves. The upper half carries two spindles at the top. At its lower part there is a shoulder. The lower half has threads cut on the outside at the top. There is a nut made to fit into this. When in position, this holds together the two halves of the bomb gastight. There is placed a circular lead gasket between the surfaces of contact of the two halves which ensures a perfect

contact. The fuel is placed in a nickel cup which is held in a wire support. This is attached to a taper pin which fits into a hole at the side of the lower half of the shell and makes contact with a metal piece insulated from the bomb by fused-on enamel. One terminal of the fuse-wire is connected to a binding screw on the pin. The other terminal is connected to a second taper pin passing through a second hole in the lower half shell. The fuse wire is so adjusted that it dips into the fuel without touching the nickel cup. The best plan is to connect the fuse wire as described and shake from

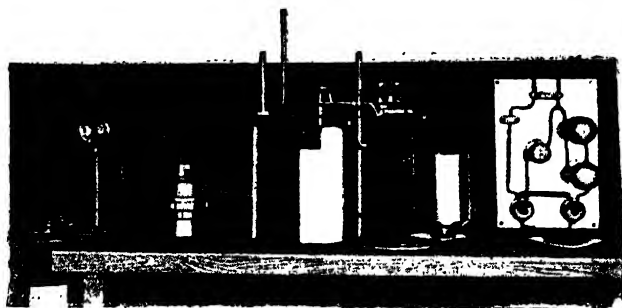


Fig. 26

a weighing bottle which contains the dried sample of coal passing through 60 mesh sieve and which has been exactly weighed, on to the nickel cup a quantity of sample judged to be about one gm. Reweigh the weighing bottle. Difference gives the exact quantity of coal transferred. 10 ml. of water are placed in the bomb. It is then covered with the upper half and the nut carefully turned by hand until it turns no more. At this stage a large wrench is used to tighten the nut. One of the spindle valves is closed. The other is opened only one turn and the oxygen from the oxygen cylinder slowly admitted. The pressure must be allowed to rise gradually. Too rapid admission of oxygen into

the bomb will blow off the fuel which will escape combustion. To avoid even the remotest chance of the solid fuel in the form of powder being blown off, there are two baffle-plates inside the upper cup. These divert the direction of flow of oxygen from the fuel-pan to the extreme side of the bomb.

A current of about 1.8 amperes is necessary for sparking the wire and about .5 ampere for running the motor for stirrer. The leads from the source of current are connected, one to the taper pin inserted into the insulated hole and the other to one of the spindles. The whole is placed in the calorimeter vessel holding 2000 gms. of water. The motor is started and the temperature noted every 30 seconds. After 5 minutes' stirring, the fuel is ignited. The temperature rise is recorded every 30 seconds. This record is continued for 5 minutes after the maximum temperature is reached.

The method of calculation will be clear from the following observations of an actual run :—

Weight of Coal 1.000 gm.

Time	Temperature	Time	Temp.	Time	Temp.
0-00	1.300°C	5-00	1.325 (Fired)	9-00	3.700
0-30	1.300	5-30	2.050	9-30	3.700
1-00	1.300	6-00	3.050	10-00	3.700
1-30	1.300	6-30	3.420	10-30	3.700
2-00	1.305	7-00	3.570	11-00	3.695
2-30	1.310	7-30	3.650	11-30	3.695
3-00	1.410	8-00	3.690	12-00	3.690
3-30	1.315	8-30	3.700	12-30	3.690
4-00	1.320	( Maximum		13-00	3.690
4-30	1.320	Temp. )		13-30	3.690

Apparent rise in temperature =  $3.700 - 1.325$   
 $= 2.375^{\circ}\text{C}.$

$$\begin{aligned} \text{Rate of change of temperature before firing} \\ = \frac{1.325 - 1.300}{5} = 0.005^\circ \text{C.} \end{aligned}$$

$$\begin{aligned} \text{Rate of change of temp. after reaching the maximum} \\ \text{temp.} = \frac{3.700 - 3.690}{2} = 0.002^\circ \text{C.} \end{aligned}$$

$$\begin{aligned} \text{Mean rate of change of temp. during run} &= \frac{+0.005 - 0.002}{2} \\ &= +0.0015^\circ \text{C.} \end{aligned}$$

$$\begin{aligned} \text{Total cooling correction} &= (\text{Time Max. temp. reached} \\ &\quad \text{minus Time of firing}) \times 0.0015 \\ &= (8.30 - 5.00) \times 0.0015^\circ \text{C.} \\ &= 3.5 \times 0.0015 = 0.005^\circ \text{C.} \end{aligned}$$

$$\begin{aligned} \text{Corrected rise of temperature} &= 2.375 - 0.005 = 2.370^\circ \text{C.} \\ \text{The water-equivalent of the bomb, calorimeter can, etc.} \\ &= 434 \text{ gms.} \end{aligned}$$

$$\begin{aligned} \text{The calorific value (without correcting for } \text{H}_2\text{SO}_4 \\ \text{+ HNO}_3\text{)} &= 2444 \times 2.37 = 5798 \text{ gm. cal.} \end{aligned}$$

The water-equivalent of the bomb, calorimeter can, etc. is ascertained by making a determination with a fuel of known calorific value. Pure cane-sugar, benzoic acid or naphthalene is used for the purpose. Assuming that the above temp. data were obtained using 2000 gms. of water in the calorimeter, 10 gms. of water in the bomb, and with a weight of 0.9136 gms. of benzoic acid as the standard combustible, then the water-equivalent will be given by the equation.

$$(2010 + w) \times 2.37 = \text{the number of gm. cal. obtained from 0.9136 gm. of benzoic acid.}$$

The calorific power of 1 gm. of benzoic acid is 6320 gm. cal.

Correction for the formation of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  :—

In the methods of firing coal, as practised, in industrial establishments, the sulphur present in it is burnt

to  $\text{SO}_2$ . The heat of formation of  $\text{SO}_2$  per formula weight is 69,000 gm. cal. In the bomb calorimeter, the sulphur gets burnt to  $\text{SO}_2$  which then dissolves in the water present in the bomb forming  $\text{H}_2\text{SO}_4$ . The heat of combustion and the heat of solution, per formula weight of  $\text{SO}_2$ , is 140,740 gm. cal. The difference in the heating value per gm. of sulphur is  $\frac{140,740 - 69,000}{32}$   
 =2242 calories.

Heat of formation of nitrogen pentoxide and the solution of this in infinite volume of water evolve  $-1200 + 29797$  ( i. e. ) 28,697 gm. cal. Two formula weights of  $\text{HNO}_3$  or 20,000 ml. 0.1N- $\text{HNO}_3$  evolve 28,697 gm. cal. Hence the formation of 1 ml. 0.1N- $\text{HNO}_3$  corresponds to 1.43 gm. cal.

The bomb washings are titrated with 0.1 N- $\text{Na}_2\text{CO}_3$  using methyl orange as indicator. The solution is treated with 2 ml. of conc.  $\text{HCl}$ , boiled and to the boiling solution is added 10 ml. of a boiling hot  $\text{BaCl}_2$  solution. ( 10% strong ). The precipitate of  $\text{BaSO}_4$  is allowed to settle for 12 hrs., filtered, washed, cooled and weighed. From the weight of  $\text{BaSO}_4$ , S is calculated. From this the number of ml. of 0.1 N- $\text{H}_2\text{SO}_4$  that can be obtained is calculated. This number is subtracted from the number of ml. of 0.1 N- $\text{Na}_2\text{CO}_3$  used. The number so obtained represents the number of 0.1 N- $\text{HNO}_3$  formed by the combustion of the nitrogen present in the air in the bomb and the nitrogen present in the coal sample. Assuming that 0.32% S is present in the coal, the number of ml. of 0.1N- $\text{H}_2\text{SO}_4$  corresponding to the sulphur present in 1 gm. sample taken for combustion equals 2.0. If the total volume of 0.1 N- $\text{Na}_2\text{CO}_3$  used for the titration of the acids is 3.7 ml., the volume of  $\text{HNO}_3$  formed is 1.7 ml. of 0.1 N- $\text{HNO}_3$ . The heat evolved during the formation of this volume of  $\text{HNO}_3$  equals  $1.7 \times 1.43$ , i.e., 2.4 gm. cal.,

The heat evolved, due to the formation of  $\text{H}_2\text{SO}_4$  from 0.0032 gm. sulphur, equals 7.2 gm. cal.

Hence the total deduction is 7.2+2.4 or 9.6 gm. cal.

The calorific value of the coal tested is 5768-9.6, i.e., 5758.4 gm. cal.

NOTES:—

( 1 ) In the case of fuel oils, the ignition wire does not dip into the oil but a strip of filter-paper 4-5 mm. wide, folded into the form of a triangle, is bent double on the wire so that the two ends dip into the oil. The paper is weighed accurately and allowance is made for the calorific value of this along with the allowance to be made for the formation of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  as shown above. A pressure of 25 atmospheres per sq. inch ( of oxygen ) is required in the combustion of oils. The calorific value of paper ( Cellulose ) per gm. is 4190 gm. calories. The following are the allowances to be made in respect of ignition wire, per gm :—

Material of the wire	gm. cal.
Iron	1600
Nickel	985.

The usual practice is to use a 3 inch to 5 inch long wire. The length of wire, left after combustion is measured off. Knowing the weight per inch of wire, allowance is made for the heat resulting from the length of wire burnt. Owing to the easy volatility of petrol, it must not be weighed out into the silica crucible. Gelatine capsule with cover supplied for the purpose is filled with petrol and weighed. This is then fired. On account of the non-uniformity of the gelatine capsules and the uncertainty therefore of their calorific values, no exact deduction can be made from the total heat obtained. Apart from this difficulty there is the fear of accidents from violent explosions. It is therefore

advisable to determine the calorific value of petrol by combustion of the oil in a special type of burner, using the Junker calorimeter. See Expt. 83.

The quantity of petrol burnt is ascertained by weighing the lamp before and after an experiment. At least 10 gms. of the oil should be burnt.

(2) The following are the calorific values of the standard combustibles in use :—

Cane-sugar	3950 gm. cal.
Benzoic Acid	6220 „
Naphthalene	9710 „

(3) The calorimeter fitted with the Mahler-Krocker bomb is in more common use in this country. Fig. 27. Unlike the Emerson outfit, this type is supplied with a screw press in which the sample of coal is compressed to form a pellet, the middle portion of the nickel ignition

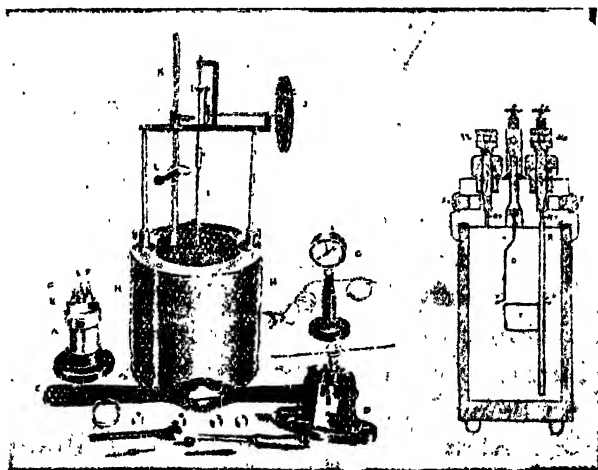


Fig. 27.

wire forming part of the pellet. This is weighed and transferred to a small silica crucible which is placed in position on its support (one of the) electrodes. These are of platinum, one a stout wire and the other a tube

of about 2.3 mm. bore. This tube reaches to within two inches of the bottom of the bomb and communicates with the spindle serving for the admission of oxygen from the oxygen cylinder. As the oxygen enters the bomb via the platinum tube and at a point below the silica crucible containing the pellet, the chances of any particles of coal being blown off to the bottom of the bomb are minimised. The admission of oxygen must always be made through this tube and not by the use of the spindle meant for the discharge of oxygen surplus and combustion products. The free ends of the nickel wire are attached to the electrodes, one end to each. One other point of difference from the Emerson type of bomb consists in the fact that the stirrer is hand-operated, though a motor for running the stirrer can be added. A stirrer is moved up and down in the Mahler-Krocker type whereas in the Emerson type, the water in the calorimeter is drawn up and discharged from above without splashing any water outside the calorimeter.

With a view to use the pressure gauge forming part of the Emerson outfit, with the Mahler-Krocker type of bomb calorimeter, the threaded and one-holed brass attachment 'A' which takes the place of the threaded nut closing the inlet valve, is screwed into position, tightened with a 2 inch long wrench and then the bomb is connected with the oxygen cylinder through the pressure-gauge. A small leather washer, moistened with a drop of water, prevents the leakage of oxygen during the filling of the bomb. A 3 inch long and  $\frac{1}{8}$  inch diameter rod, nickel-plated, serves to open and close the spindles for the admission of oxygen and the discharge of the products of combustion. As in the Emerson



bomb, only one turn of the spindle is necessary whether for admission or discharge of gas. Quick manipulation is necessary when the pressure of 300 lbs. has been indicated.

The oxygen cylinder valve is closed first and then immediately the spindle valve on the bomb. This is then detached from the pressure gauge, the attachment 'A' to the bomb removed, the normal nut put in its place on the bomb, and the whole then introduced into the calorimeter. The current necessary for ignition of the fuse wire is about 1.8 amperes. Further manipulations are from this point the same as with the Emerson bomb.

The following modified method of correction for radiation losses is reproduced in full from Rec. Geo. Survey of India, Vol. LXIII, Part II, because of the stress laid by the Indian Coal Grading Board on the uniformity of methods of testing coal.

Time minutes	Temperature °C.
0	1.601
1	1.603
2	1.607
3	1.610
4	1.612
5	1.620
Coal ignited	
5½	1.880
6	2.770
6½	3.190
7	3.302

$7\frac{1}{2}$	3.350
8	3.360
$8\frac{1}{2}$	3.367
9	3.368 ( Maximun )
10	3.360
11	3.348
12	3.335
13	3.320
14	3.302
15	3.290

In the first period of five minutes the temperature rises from  $1.601^{\circ}\text{C.}$  to  $1.620^{\circ}\text{C.}$  giving an average of  $0.0038^{\circ}\text{C.}$  per minute. As the correction is made for cooling this is taken as a cooling rate of  $0.0038^{\circ}\text{C.}$  at the temperature of  $1.61^{\circ}\text{C.}$ , i.e., the average of the two extremes. Similarly the cooling rate in the final period of five minutes is  $0.0140^{\circ}\text{C.}$  at the temperature of  $3.325^{\circ}\text{C.}$  ( i.e., the mean of  $3.360^{\circ}\text{C.}$  and  $3.290^{\circ}\text{C.}$  ). During each of these periods of five minutes the rate of cooling is taken as constant, while for the intermediate temperatures the rate of cooling is taken from a graph. The graph, as shown below, is a straight line drawn between two points representing the two rates of cooling just calculated.

The rate of cooling taken for each minute is that corresponding to the observed temperature at the half-minute. Thus during the sixth minute the observed temperature rises from  $1.620^{\circ}\text{C.}$  to  $2.770^{\circ}\text{C.}$  and the effective mean is taken as  $1.880^{\circ}\text{C.}$ , which is the observed temperature at  $5\frac{1}{2}$  minutes.

The following corrections are thus made :-

Time minutes	Observed temperature °C.	Correction for one minute °C.	Total correction °C.	Corrected temperature °C.
0	1.601	nil	nil,	1.6010
1	1.603	-0.0038	-0.0076	1.5994
2	1.607	-0.0038	-0.0376	1.5994
3	1.610	-0.0038	-0.0114	1.5986
4	1.612	-0.0038	-0.0152	1.5598
5	1.620	-0.0038	-0.0190	1.6010
6	1.880(at $5\frac{1}{2}$ )	-0.001	-0.020	...
7	3.190(at $6\frac{1}{2}$ )	-0.0125	-0.0075	...
8	3.350(at $7\frac{1}{2}$ )	-0.0140	-0.0065	...
9	3.367(at $8\frac{1}{2}$ )	-0.0140	0.0205	...
10	3.360.	0.0140	0.0345	3.3945
11	3.348	0.0140	0.0485	3.3965
12	3.335	0.0140	0.0625	3.3975
13	3.320	0.0140	0.0765	3.3965
14	3.302	0.0140	0.0905	3.3925
15	3.290	0.0140	0.1045	3.3945

The object of applying the cooling correction is to eliminate any errors arising from heat entering or leaving the calorimeter and, therefore, if the temperature at each point could be determined with complete accuracy, it is evident the six initial temperatures calculated would all be identical, as would also the six final temperatures. Actually they are not identical giving some measure of the error inherent in reading the thermometer. The error is, however, reduced by taking the mean of each series of temperatures so that the system of correction serves a double purpose. The calorific value is calculated as follows :—

Mean of corrected final temperatures =  $3.3953^{\circ}$  C.

Mean of corrected initial temperatures =  $1.5993^{\circ}$  C.

	Rise	<u><math>1.7960^{\circ}</math> C.</u>
Weight of coal	0.884	gramme
Weight of water	2.500	grammes
Water equivalent	<u>780</u>	grammes
Total weight of water	3.280	grammes
Calorific value	$3.280 \times 1.796$	gm. cal.
	<u>0.884</u>	
	=6,665 gram calories.	

If the calorific value were determined without taking into consideration the cooling correction, it would be 6,486 gm. cal.

4. The thermometer in use for this purpose is the Beckmann thermometer. The scale extends over  $6^{\circ}$  C. and the position of the mercury on the scale can be adjusted by removing from the bulb or adding to it small quantities of mercury. For this purpose a device is contained in the top of the thermometer, consisting in effect of an enlarged portion of the capillary bore of the thermometer. If the thermometer bulb is warmed, mercury flows into this space; and if the thermometer is inverted and tapped, the thread is broken off at this point and on cooling, the thread retracts and the bulb contains less mercury than it did before. Conversely, if the thermometer is set upright and the bulb allowed to cool, after joining up by warming with the thread in the reservoir more mercury flows into the bulb from the reservoir. The thermometer, therefore, although of short range, can be used for any ordinary temperature. The readings recorded, however, are arbitrary and have no relation to actual centigrade degrees in the absolute sense, although a difference of one degree is approximately the same as a difference of one degree in the centigrade scale proper. <sup>3</sup>

5. When the pressure of oxygen from a cylinder which has been in continuous use is not high enough to permit filling the bomb at the specified pressures ranging from 300 to 375 lbs. per sq inch, the practice is to fill the bomb first with oxygen from the low pressure cylinder and then from the high pressure cylinder. This leads to economy in the use of gas. The pre-war price per c. ft. of gas at N. T. P. was annas four.

6. No parts of the bomb are to be greased or oiled.

7. One of the connecting wires forming part of the electric circuit for ignition of the fuse-wire is connected to a terminal binding post insulated from the bomb by fused-on enamel. The other wire is connected to a second binding post. In this way short circuiting and failure of ignition is guarded against.

8. The readings of the thermometer are taken with a magnifying glass.

## EXPERIMENT 82.

### Determination of Phosphorus in Coal ash.

#### Principle :—

This is the same as that underlying the determination of this element in iron or steel. Coal ash consists of the silicates and phosphates of calcium, aluminium and titanium.  $\text{SiO}_2$  is eliminated by treatment with  $\text{HF}$  and  $\text{HNO}_3$ . The titanium in the residue is eliminated by fusion with  $\text{Na}_2\text{CO}_3$ . The fused mass is treated with water and filtered. The filtrate contains all the phosphorus. This is acidified with  $\text{HNO}_3$  and treated with  $(\text{NH}_4)_2\text{MoO}_4$ . The ppt. of phosphomolybdate is filtered off and titrated with 0.1 N— $\text{NaOH}$  Solution. See Expt. 16.

Ash 5 gms. of coal in a platinum basin in a muffle furnace at  $750^\circ$  to  $800^\circ\text{C}$ . Cool. Add 10 ml. conc.  $\text{HNO}_3$

and 5 ml. HF. Repeat evaporation to dryness with 5 ml. more of conc.  $\text{HNO}_3$ . Ignite gently. Fuse the residue with 3–4 gms. of  $\text{Na}_2\text{CO}_3$ . Extract the melt with water, and transfer to a 150 ml. evaporating basin. Heat the extract to  $90^\circ\text{--}95^\circ\text{C}$ . Filter. Wash with  $1\%$   $\text{Na}_2\text{CO}_3$  solution and finally with water. To the filtrate add conc.  $\text{HNO}_3$  until acid and then 10 ml. more. Add 50 ml. of ammonium molybdate (Johnson's reagent) and finish as in Experiment 16.

NOTES :—

(1) When the  $\%$   $\text{TiO}_2$  is high in the ash, it is necessary, for very great accuracy, to fuse the residue obtained by filtering off the melted extract with  $\text{Na}_2\text{CO}_3$  a second time and adding the filtered extract to the first portion and then proceed to the precipitation as phosphomolybdate. In a sample of coal used for coke making the ash contained 0.76% P and 1.36%  $\text{TiO}_2$ .

(2) Fusion with  $\text{Na}_2\text{CO}_3$  yields  $\text{Na}_3\text{PO}_4$  and  $\text{Na}_4\text{TiO}_4$ . Of these the former is soluble in water whereas the latter changes to  $\text{Na}_2\text{TiO}_3$ , when the temperature is raised to  $90\text{--}95^\circ\text{C}$ . and becomes insoluble.

(3) Vanadium has a retarding action and is precipitated along with the phosphorus. Its presence is detected by the formation of a reddish-brown colour with  $\text{H}_2\text{O}_2$ . To test for its presence proceed as follows:—

Fuse about 0.1–0.2 gm of the ash with 2 gms. of  $\text{Na}_2\text{CO}_3$  and 0.1 gm of  $\text{KNO}_3$  in a platinum crucible. Leach with hot distilled water. Nearly neutralize with dil.  $\text{HNO}_3$  (s. g. 1.2) and evaporate to dryness. Treat the residue with hot water, filter, acidify the filtrate with dil.  $\text{H}_2\text{SO}_4$ . Cool, and add 2–3 ml. of  $\text{H}_2\text{O}_2$ . A reddish-brown colour shows the presence of vanadium. If it is present, its interference can be entirely prevented by the addition of 40

ml. of conc.  $\text{HNO}_3$  prior to the addition of 50 ml. of Johnson's reagent. See Expts. 14, 16 and 17. The precipitate of ammonium phosphomolybdate must be washed free of nitric acid with a 1% solution of  $\text{KNO}_3$ , and the alkalimetric titration then adopted.

### EXPERIMENT 83.

#### Determination of Nitrogen in Coal.

##### Principle :—

When a sample of coal is heated with conc.  $\text{H}_2\text{SO}_4$ , all the nitrogen in the substance is converted into ammonium sulphate. This is estimated by pouring into the mixture caustic soda solution, distilling off the ammonia and absorbing the same in a measured excess of standard sulphuric acid. The excess is titrated. The volume of the acid used is a measure of the amount of ammonia and therefore of nitrogen in the sample.

##### Procedure :—

Weigh 1 gm. of the coal sample ground to pass through a 100 mesh I. M. M. sieve into a 500 ml. Kjeldahl flask. Add 30 ml. conc.  $\text{H}_2\text{SO}_4$ , 5-8 gms.  $\text{K}_2\text{SO}_4$  and 0.6 gm. (one small globule) of mercury. Boil until colourless (2-3 hours). Allow to cool. Add a few small crystals of  $\text{KMnO}_4$ . Boil for 1 hour more. Cool. Pour into a 750 ml. round-bottomed flask containing 100 ml. water. Wash 3 or 4 times with water and transfer to the round-bottomed flask. Introduce 25 ml. of a solution of  $\text{K}_2\text{S}$ , containing 40 gms. of the solid to the litre, to precipitate the mercury in the mercuric sulphate as  $\text{HgS}$ . Next add 75-100 ml. of a strong solution of caustic soda (50%). Introduce powdered pumice about  $\frac{1}{2}$  gm. and connect as shown in Fig. 15 b. (p. 207). The receiver 'D' contains 50 ml. 0.1

$N-H_2SO_4$ . Distil until about 200 ml. distil over. Titrate the excess of  $H_2SO_4$  against 0.1  $N-NaOH$  using methyl orange as indicator.

NOTES :—

(1) The oxidation of the organic matters of the coal substance is helped by the introduction of mercury. Mercuric sulphate is formed by the action of conc.  $H_2SO_4$  at the boiling temperature of mercury. This is reduced to mercurous sulphate by the carbonaceous matter. This again passes into mercuric sulphate by the oxygen liberated from the reaction mixture. The cyclic process of oxidation and reduction continues until all the coal is oxidised. The Fuel Research Board, England, recommends the use of mercuric oxide. It does not advise the addition of  $KMnO_4$ , but it recommends boiling the solution 2 hours after it becomes colourless.

(2) The addition of  $K_2SO_4$  has the effect of raising the boiling point of the reaction mixture, at which temperature the oxidation of the coal substance takes place more quickly.

(3) If the catalytic mercury is not removed as sulphide by the introduction of  $K_2S$ , it will combine with  $NH_3$  which is liberated on the subsequent addition of  $NaOH$ . The ammonia combining with mercury forms compounds which are not decomposed by  $NaOH$  and will not therefore be estimated.

(4) It is important that no  $NaOH$  is carried over into R during distillation either as splash or mechanically. The use of the splash head prevents this very effectively. Zinc dust (1 gm.) may be substituted for pumice powder to prevent 'bumping' during distillation.

(5) A blank determination, substituting pure cane



sugar for the coal sample, gives the data necessary to supply a correction for nitrogen compounds in the reagents used.

(6) When selenium is used as a catalyst in place of mercury, the conversion of nitrogen into ammonium sulphate is accomplished in about half the time. The details of the process using selenium are the same as above except that  $K_2S$  is omitted.

#### EXPERIMENT 84.

##### Ultimate Analysis of Coal.

##### Determination of Carbon and Hydrogen.

##### Principle :—

As in the analysis of organic substances, the determination of carbon and hydrogen in coal is carried out by the oxidation of these elements into  $CO_2$  and  $H_2O$  respectively and the absorption of the same in suitable media, KOH solution for the former and anhydrous  $CaCl_2$  for the latter. The tubes containing these reagents are weighed before and after an experiment. The oxidation is effected by passing a current of oxygen over the heated material in a combustion tube. The temperature at which oxidation takes place is  $800-850^\circ C$ . As the volatile matter liberated from coal at that temp. is evolved rapidly and is likely to be carried off to zones of the combustion tube where the temp. is not high enough to burn the hydrocarbon gases and hydrogen, a layer of granulated copper oxide is kept in the zone where a temp. of  $800$  to  $850^\circ C$ . prevails. In its passage through this layer, the volatile matter gets completely oxidised. The fixed carbon in the coal is also converted into  $CO_2$ .

##### General remarks :—

Elaborate precautions have to be taken to free the oxygen introduced for combustion from carbon-di-

oxide and moisture. This is accomplished by what is known as the 'purifying train' of wash bottles containing KOH solution and conc.  $\text{H}_2\text{SO}_4$ . With a view to maintain the same degree of dryness in the gases entering the combustion tube as in the gases leaving the 'absorption train' of U tubes charged with granular calcium chloride and caustic potash solution, the former train, namely, the purifying train, also contains U tubes charged with soda lime and granular calcium chloride.

As the tubes forming the units of the absorption train are weighed, before the experiment, filled with air, it is necessary to weigh the same, after an experiment, filled with air and not oxygen. This necessity arises from the fact that the U tubes will have each a volume of about 50 ml. and the increase in weight of the same when filled with oxygen will be about 0.01 gm more than when filled with air. This increase will introduce an error of about 10-15% in the hydrogen, and of about 2-5% in the carbon determination. The purifying train must therefore consist of a duplicate series of wash-bottles charged with KOH, conc.  $\text{H}_2\text{SO}_4$ , and granular calcium chloride in order to dry the air which is introduced into the combustion tube, on completion of the combustion using oxygen.

#### **Apparatus :—**

The combustion is effected in a hard glass or silica tube. The tube is heated in a furnace heated by gas or electricity. On account of ease of manipulation, electric furnace is more commonly used. This consists of three sections each with its own resistance coil and rheostat. The dimensions of the tube, the three sections of the furnace, the frame on which they are supported

and can be moved, are shown in Fig. 28. The charge in the tube beginning at the end connected to the purifying train is approximately as follows :—

5 cm. space.

10 cm. oxidised copper gauze spiral through which passes a stout copper wire provided with a loop for convenience in withdrawal.

10 cm. space for boat.

45 cm. of granular copper oxide held in position by rolls of oxidised copper gauze 1 cm. long.

10 cm. of fused granular lead chromate followed by a roll of oxidised copper gauze freshly reduced 1 cm. long.

5 cm. silver spiral.

8 cm. space.

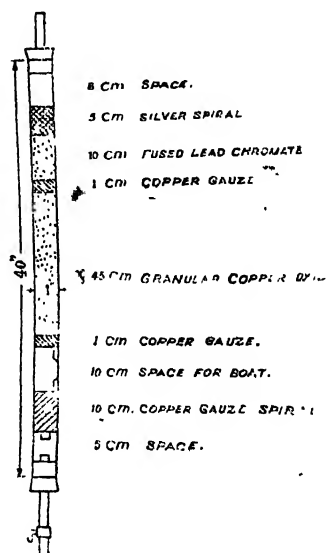


Fig. 28.

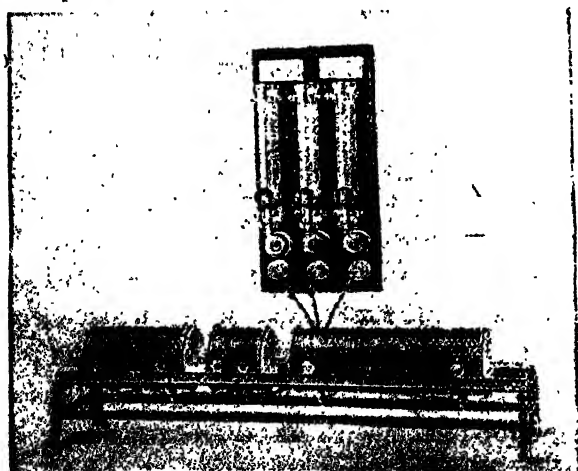


Fig. 28.

The purifying train is made up of two wash bottles

one of which is charged with KOH solution ( one part by weight of the sticks in one part by weight of water ) and the other with conc.  $\text{H}_2\text{SO}_4$ , followed by U tubes charged with soda lime and granular calcium chloride. Two such trains, connected to the combustion tube by a three-way tap or a similar device permit of the use of dry oxygen or air as required.

The three-way tap is connected to the combustion tube by indiarubber tubing attached to a glass tube of  $1\frac{1}{2}$ -2 mm. bore passing through a well-fitting rubber stopper.

The absorption train, which is connected directly to the other end of the combustion tube by a well-fitting rubber stopper consists, in the order named, of ( a ) a U tube charged with granular  $\text{CaCl}_2$  and ( b ) potash bulbs, containing an aqueous solution of KOH ( 1 part by weight of the solid in 1 part by weight of water ), and fitted with a small side tube charged with granular calcium chloride.

Before use, the combustion tube is heated in a current of oxygen, maintaining the copper oxide at a temp. not below  $800^\circ\text{C}$ . and the lead chromate at a dull red heat (  $600$ - $650^\circ\text{C}$ . ) ; if the change in weight of the calcium chloride tube and potash bulbs at the end of half an hour does not exceed  $0.0005$  gm., the apparatus may be considered to be in proper condition. The oxygen in the tubes should be displaced by air and the weighing then made.

The quantity of the finely powdered coal used is  $0.2$ - $0.3$  gm. spread evenly over the bottom of a porcelain or silica boat about 8 cm. long.

The ash remaining in the boat at the end of an experiment should be examined carefully to ascertain whether any carbon has escaped combustion.

## NOTES :—

## ( 1 ) The Absorption tube for Moisture.—

As the granular calcium chloride will absorb carbon di oxide in addition to water vapour, it should be saturated with the gas and subsequently freed from the excess of the same before using, by passing a current of dry air through it. The power to absorb  $\text{CO}_2$  arises from the fact that in the preparation of the anhydrous form, the substance is heated to about  $800^\circ\text{C}$ . at which temp. a slight decomposition takes place with the formation of  $\text{CaO}$  which absorbs  $\text{CO}_2$ .

## (2) The Absorption Apparatus for Carbon dioxide.—

Instead of potash bulbs, U tubes charged with freshly prepared soda-lime may be used for absorbing the carbon dioxide. Sodalime is prepared by slaking lime with a solution of sodium hydroxide ( 50% ) and heating the slaked product to about  $420^\circ\text{C}$ . The mass clots up. This is cooled, broken up and sieved.

( 3 ) The results for carbon will be inaccurate if the determination of any carbonates present in coal is not made and allowed for.

## (4) Water of constitution in Inorganic constituents.—

The results for hydrogen will be inaccurate on account of the fact that the water of constitution present in the inorganic constituents is expelled at the temp. employed for combustion. No reliable method exists for its determination. However an approximate correction can be made if the quantitative composition of the ash is known.

( 5 ) To ensure complete combustion, the temperature of the copper oxide should not fall below  $800^\circ\text{C}$ .

( 6 ) The oxidised and freshly reduced copper gauze inserted after the layer of fused lead chromate is for the purpose of reducing oxides of nitrogen to nitrogen. If this is not done, the results for carbon will be high. The copper gauze at the back end of the combustion tube, i.e., the end near the purifying train, is for preventing any volatile products from diffusing into the soda-lime and  $\text{CaCl}_2$  U tubes.

( 7 ) The lead chromate serves to oxidise  $\text{SO}_2$  to  $\text{SO}_3$  and to fix the same as lead sulphate. If the temp. in the region of the lead chromate exceeds  $650^\circ\text{C}$ .,  $\text{SO}_3$  will pass off unabsorbed.

( 8 ) The silver spiral is for combining with any chlorine that may be liberated.

( 9 ) The layer of copper oxide serves to help the complete combustion of the volatile matter evolved from coal.

( 10 ) The originator of the method for the analysis of organic substances is Liebig. His method has been applied to the analysis of coal also. It has been modified by Dennstedt. The chief features of the modified method lie in the employment of:—



Fig. 28 a.

(a) Two streams of oxygen, accomplished by the use of the apparatus shown in Fig. 28 a; these two are known as the 'Vaporising stream' and the 'Combustion stream'. The former carries forward the volatile matter from the coal to a platinum contact star (Fig. 28 b.) and the latter effects the combustion of this matter in the presence of the platinum catalyst.

(b) A mixture of lead peroxide and minium in porcelain boats in place of the fused lead chromate in the combustion tube itself. This modification serves to increase the life of the latter.



Fig. 28 b.

(c) A wash-bottle containing palladious chloride solution at the end of the absorption train. This serves to reveal the presence of carbon monoxide by the formation of a cloudiness. If this is noticed, the determination must be repeated employing a higher temperature in the furnace in the region of the contact star, i. e. the combustion zone.

(11) A desirable rate of passing the gas will be 2-3 bubbles per second.

(12) In charging the wash-bottles with conc.  $\text{H}_2\text{SO}_4$  and KOH solution, care should be taken not to bring them into contact with the neck of the bottles. If any is brought, it should be wiped off first with a damp cloth, next with a dry cloth and finally greased with vaseline. If these precautions are not taken, the stoppers will seize the neck and it will be impossible to

remove them without breaking them; These precautions should also be observed in emptying them prior to recharging.

( 13 ) The apparatus should be tested for airtightness before an analysis is undertaken. This is carried out by slipping a piece of rubber tubing on to the guard tube at the end of the absorption train and closing it by means of a pinch clamp as a stream of oxygen is passing through the wash-bottles of the purifying train. Air tightness is indicated by no bubbles passing through the potash bulbs.

( 14 ) The oxygen source is from a Pepys' gas-holder, which in turn has been filled with oxygen from a cylinder of the compressed gas. For method of filling the gas-holder, see Expt. 24. The pressure in the holder must be such that gas will be drawn in by means of the aspirator bottle at the rate of 2-3 bubbles per second through the potash bulbs of the absorption train. The screw-clip on the aspirator bottle must be adjusted to give this rate of bubbling.

( 15 ) When not in use, the absorption train units must be plugged up by means of glass rods inserted into short lengths of rubber tubing, to prevent the spoiling of the reagents.

( 16 ) The increase in weight of the calcium chloride U tube ( known as the Marchand tube ) represents the weight of water formed from which the hydrogen content of the coal sample is calculated. The increase in weight of the potash bulbs (the Geissler bulbs or the U tube ) represents the weight of  $\text{CO}_2$  from which the carbon content is calculated.

( 17 ) On account of the resistance offered by the



packing in the combustion tube to the passage of oxygen or air, the aspirator bottle is necessary. Passing oxygen directly from a cylinder of the compressed gas will lead to mechanical loss of particles and the carrying of the same from one unit of the absorption train to another and thus vitiate the results.

(18) In America, the Fleming tube charged with 'ascarite' for the absorption of  $\text{CO}_2$  is in extended use. When this tube is used, oxygen from a cylinder of the compressed gas may be passed through the combustion tube after attachment of the regulating and reducing valve to reduce the pressure to a rate of bubbling of 2-3 bubbles per second through the wash-bottles of the purifying train.

(19) As no satisfactory direct method for the determination of oxygen is available, it is obtained by difference. The percentages of the other constituents are added up and subtracted from 100.

## EXPERIMENT 85.

### Determination of the Caking Index.

#### Definition :—

The Caking Index of coal is the number of gms. of sand, electrode carbon or other inert material that can be bound together by one gram of coal to a coherent mass which will bear a 500-gram weight without crushing. The percentage of uncemented loose powder should not be more than 5, when the coherent mass stands the 500-gm. weight. This test is known as the Campredon test, though the original method due to Campredon has been modified.

#### Procedure :—

1. Weigh the requisite quantities of finely powdered

coal and sand to give exactly 25 gms. of a mixture, having the two ingredients in the desired proportions, in a tared, stoppered, cylindrical weighing bottle. Mix thoroughly and transfer the mixture to the crucible; rotating the bottle continuously during the process to prevent separation of the constituents of the mixture.

Place the charged, covered crucible on a platinum or nichrome wire triangle, so adjusted that the bottom of the crucible is at a distance of 1 cm. above the top of the Meker burner, heat the crucible for 7 minutes in the full flame and allow it to cool.

Place a smooth cork on the surface of the coked mass, lay on the top of the cork a tared, shallow porcelain dish, bottom up, and invert the whole arrangement. Remove the crucible carefully, place the coked mass on a level surface and lower the 500-gram weight gently upon it. Weigh the powder which remains in the porcelain dish.

#### NOTES :—

To obtain results which are fairly concordant when working on the same sample of coal, compliance with the following conditions is necessary :—

- (a) the size of the crucible should be the same ;
- (b) the temperature at the bottom of the crucible should be  $1000^{\circ}\text{C}.$  ;
- (c) and the sand to be used should pass through a 40 mesh sieve and be retained on a 50 mesh sieve.

Condition (b) is secured by the employment of Meker burner No. 4, diameter of grid being 3 cms.

### EXPERIMENT 86.

#### Laboratory Carbonisation Assay of Coal.

The ordinary laboratory methods of proximate and

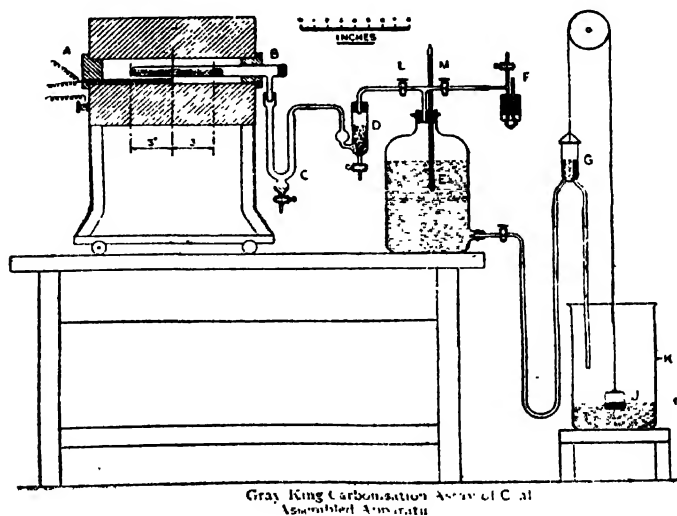
ultimate analysis of coal supply no direct information as to the quality and quantity of the gaseous and liquid products of carbonisation, as to the rate of evolution of these products at different temperatures, or as to the influence of temperature and time of carbonisation on the qualities of the resulting coke.

When such information in regard to a coal is required the following methods for the assay of coal have been recommended by the Fuel Research Board, England :—

1. the Gray-King apparatus ;
- and 2. the Lessing apparatus.

### **Description of the Gray-King Apparatus :—**

The assembled Gray-King apparatus is represented diagrammatically in Fig. 29 and scale drawings of certain of the parts are shown in Fig. 30. This is suitable for the examination of the products of coal carbonisation at temperatures of about  $600^{\circ}\text{C}$ .



**Fig. 29,**

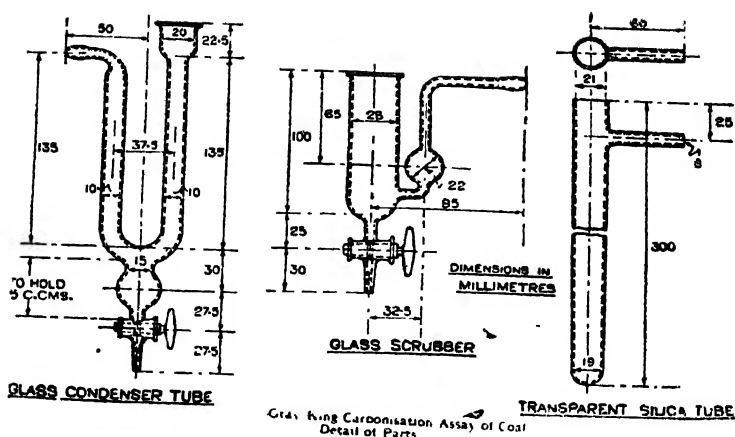


Fig 30.

The furnace 'A' may be gas fired, but is, more conveniently, a nichrome-wound electric furnace, giving a uniformly heated space at least 15 cms. long at the centre ; the temperature is regulated with a thermocouple, the junction of which is in contact with the outside of the retort tube at the middle of the furnace.

The hard glass or silica tube 'B' is approximately 30 cms. long and has a diameter of about 2 cms ; the short side-tube of about 8 mm. diameter, is sealed in at a distance of about 2 cm. from the open end, which is closed by a rubber stopper. The tube should be smooth and of uniform bore, or may preferably have a slight taper, so that it is slightly wider at the open end.

The U tube 'C', which acts as a condenser and may be externally cooled, has an extension with a capacity of at least 5 ml. for the collection of the liquid products.

The tube 'D', of diameter 2 or 3 cm. by 15 cm. long is charged with glass beads drenched with sulphuric acid, for the absorption of ammonia.

The gasholder 'E' filled either with a mixture of equal volumes of glycerine and water or with an almost saturated aqueous solution of magnesium chloride or with water saturated with the coal gas from a previous experiment, is connected to a glass reservoir 'G' by means of a rubber tube ; this reservoir is suspended by a cord passing over a pulley and counterbalanced by a glass vessel containing lead shot. As gas enters 'E', the displaced liquid passes into 'J' and overflows into the tank 'K' in which the counterpoise 'J' floats. If 'E' and 'K' have the same diameter, a fall of level in the former causes an equal rise in the latter, and the movement of the float 'J' lowers 'G' to the same extent, thus maintaining automatically a constant pressure in the gas holder. By adjustment of the vessel 'K' or of the pulley, at the beginning of the experiment, so that the level in 'G' is below that of the liquid in 'E', any desired difference of level may be maintained steadily throughout the test, provided that the connecting tube is of sufficient diameter to allow the liquid to pass freely from 'E' to 'G'.

### **Method of Operation :—**

The coal sample is ground to pass through a 60 mesh I.M.M. sieve and is dried, in an inert gas if necessary, at 105-110°C. The gas holder is charged with liquid up to the level of the bottom of the rubber stopper, the reservoir 'G' is adjusted so that the top of the overflow tube is about 1 cm. below the level of the liquid in 'E' and the clean dry U tube 'C' is weighed and attached as shown in the figure. The tube 'B', together with a small quantity of previously ignited asbestos wool for use as a plug, is weighed to the nearest centigram and is charged with 20 gms. of dry coal, spread out in an even layer occupying about two-thirds of the diameter of the tube, and held in position

by the asbestos, which is inserted as a loose flattened plug to allow of the free passage of gas. The charged tube is then connected to 'C' by means of a rubber stopper, and clamped into position with a slight forward slope. The furnace, previously heated to  $300^{\circ}\text{C}.$ , is then pushed forward into the position shown.

As soon as the evolution of expanded air and of gas occluded by the coal stops, the temp. of the furnace is gradually raised by cutting out resistance in the external circuit so that the ultimate temp.,  $550^{\circ}\text{C}.$  or  $600^{\circ}\text{C}.$ , is reached at the end of an hour. During this period, observations are made of the temperatures at which oil appears and at which the gas evolution commences.

Heating at the final temp. is continued during an hour, at the end of which time the rate of evolution of gas has fallen so low that further heating gives a negligible addition to the volume; the furnace is now withdrawn, the tube 'B' is allowed to cool, the pressure shown on 'F' is adjusted to zero, the stopcocks 'L' and 'M' are closed and 'B' is opened.

The yield of coke is arrived at by weighing 'B' when cold. After weighing, any tar is removed from the end of tube 'B' by means of solvents like petroleum ether, toluene, xylene, etc., and the tube is then reweighed; the loss of weight is reckoned as tar and added to the weight of tar collected in 'C'. The coke yield is calculated from the weight of the cleaned tube.

From the increase of weight of 'C' the total yield of tar and liquor is obtained. In order to obtain the separate yields, the contents of 'C' are washed into a 10 ml. graduated cylinder with toluene, the volume of the aqueous portion measured, and then converted into gms. For this purpose the specific gravity of the aqueous solution is taken as 1. If it is difficult to obtain an

accurate measurement of the volume of the aqueous portion, owing to the meniscus not being clearly defined, the contents of 'C' from a second test are washed into a 100 ml. distillation flask with 50 ml. of toluene, and the whole gently distilled until 25 ml. have been collected in a Sutherland flask calibrated for a water-toluene meniscus. The volume of the aqueous portion can then readily be measured.

The contents of 'D' are washed into a flask, mixed with the aqueous liquor from 'C' from the first test, and distilled to give the yield of ammonia. 5 ml. of a 50% NaOH solution should be added, before commencing the distillation in order to decompose ammonium compounds. A splash head should also be used as in Expt. 93.

To ascertain the gas volume, water is removed from 'k' by means of a pipette and is allowed to flow into 'G' which is gradually raised till the top of the inlet is on the level of the liquid in 'E' and the liquid in 'F' is at a level gauge, any unused water being returned to 'K'. From the weight and the specific gravity of the water or solution collected in 'K', the volume of gas at the observed temp. and the prevailing atmospheric pressure, may be calculated.

The gas prepared in the first is generally contaminated to some extent with air, and, if more than one experiment is carried out, the gas from the first should be used to displace the air from the apparatus. This can readily be done by driving the contents of 'E' back through the open end of 'B'. The gas produced in the second test is then relatively free from air and may be used for analysis and for the determination of specific gravity. If only one test is carried out, these

determinations may be made on this gas, but due correction must be made for the amount of air included, which amounts to 5-8%.

The following example illustrates the method of reporting :—

---

Yields Per 100 gm. of dry coal—				
Coke	...	...	...	gm.
Tar	...	...	...	gm.
Liquor	..	..	...	gm.
Gas	...	..	..	gm.
Total	...	...	...	gm.
Ammonia	...	...	...	gm.
Gas ( at 60°F. and 30-in.				
saturated )	..	...	ml.	
	sp. gr. ( air= 1 )			

---

Calculated yields per ton of dry coal.				
( Assume sp-gr. of tar and liquor as 1 )				
Coke	..	..	...	cwt.
Tar	..	..	...	gals.
Liquor	..	..	...	gals.
Gas ( at 60°F. and 30 in saturated )	c. ft.			
Ammonia	..	..	...	lb.
Character of coke—				
Behaviour on distillation—				
First appearance of oil	}			deg. C.
Vapour .. ..				
Start of evolution of gas.				deg. C.

### EXPERIMENT 87.

#### The Lessing Apparatus.

##### Description of Apparatus :—

The apparatus consists of an electric furnace capable of accommodating two cylindrical quartz glass retort tubes with walls of uniform thickness and having definite dimensions, which should be strictly adhered to.



A tube of alundum or similar material, 18 mm internal dia. by 55 mm. high with a longitudinal slit 10 mm. wide is used to prevent cooling of the upper portion of the retort, with consequent condensation of tar. This fits into a circular opening in the top of the furnace which has an extra thickness of asbestos. The tube also serves as a guide when the retort is introduced into the furnace. It should not be placed in position until just before the retort is inserted. With the type of retort shown in Figs. 31 and 32, all classes of coals, including highly swelling coals, may be carbonised without difficulty.

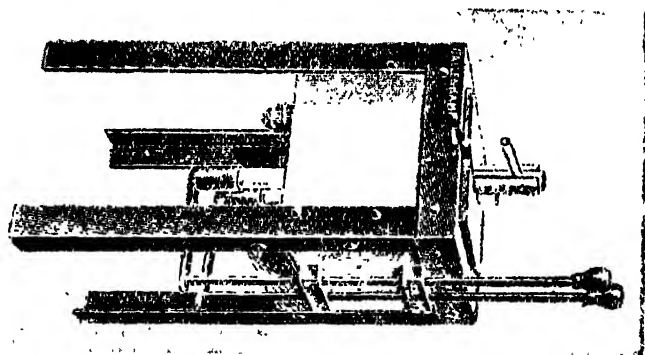
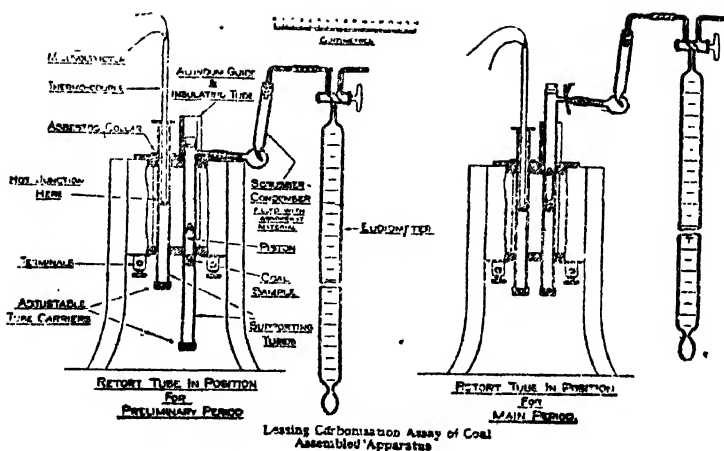


Fig. 31.



ig. 32.

The coal sample is compressed during heating by a quartz piston loosely fitting in the retort tube, so that only gas and tar vapour, but no coal dust, can pass between it and the retort wall. The position of the retort tubes in the furnace can be fixed by a height adjusting attachment which carries two plain inverted silica tubes on which the retort tubes rest. The gas passes from the retort tube by means of a side tube through a small scrubber-condenser filled with cotton wool, in which the tar is retained, into a eudiometer of about 300 ml. capacity, provided with a levelling vessel of at least equal capacity. The standard shape and dimensions of the various parts are shown in Fig. 33.

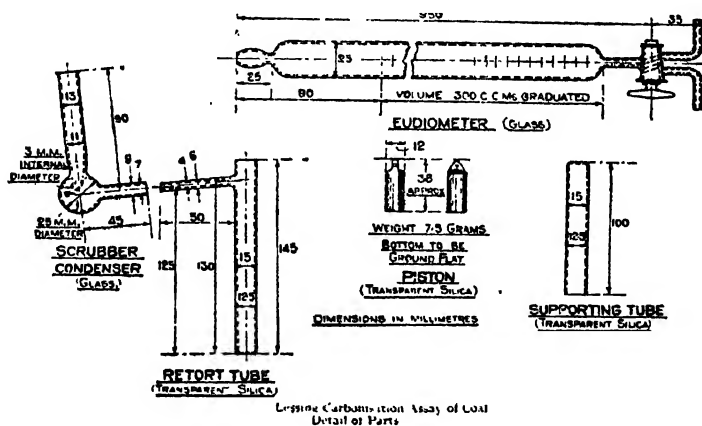


Fig. 33.

### Method of Operation :—

One gram of the air-dried sample; ground to pass through a 60-mesh I. M. M. sieve, is placed in the retort tube which has been previously weighed. The piston is then gently inserted, care being taken that the escaping air does not carry with it any coal dust, which might get jammed between the piston and the retort wall. The tube is closed with a rubber stopper. The side tube of the scrubber-condenser, fitted with a rubber

connection is then slipped over the retort side tube so that the gas cannot come into contact with the rubber tube. The scrubber-condenser, filled with cotton wool, kieselguhr or other absorbent material should be previously dried at  $100^{\circ}\text{C}$ . and weighed. It is connected by means of a rubber stopper and narrow glass tube to the inlet of the eudiometer tube, which is filled with a mixture of equal parts of glycerine and water, or a saturated solution of sodium chloride. The eudiometer is clamped in a retort stand, and it is quite safe to allow the scrubber and retort tube to be suspended freely by means of their rubber connections.

Whilst charging the retort tube with the coal sample and connecting up the various parts, the furnace is brought to the requisite temp.. It is advisable to do this before beginning the test, instead of allowing the coal to be heated slowly when starting from cold. The temperature of the furnace is adjusted by means of an outside resistance and is controlled by inserting a thermocouple into an empty retort resting in one of the tube spaces, the vacant heating space being covered by an asbestos disc. For exact work, the thermocouple should be transferred several times from one side to the other in order to check any variations between the two tubes.

Any clearance between the retort or supporting tubes and the top and bottom openings of the furnace should be covered by a closely fitting asbestos collar.

As soon as the temp. is constant, the liquid in the eudiometer is brought to the top by turning the three-way tap so as to connect with the atmosphere, and fixing the levelling bottle at a suitable height. Connection is then established between the retort and the eudiometer by turning the three-way tap into the correct position. The alundum tube is then placed in position

and the supporting quartz tube is lowered out of the furnace. The retort is then quickly inserted in the furnace so that the side tube rests on the side of the furnace and a length of 10 mm. which contains the coal charge, projects out of the bottom of the furnace. In this position the whole of the retort is preheated while the coal charge is only slightly warmed. At the end of one minute in the  $900^{\circ}$  C. test, or at the end of two minutes in the  $600^{\circ}$  C. test, the retort is raised by manipulating the supporting tube and eudiometer clamp, so that the bottom of the retort is 45 mm. above the lower level of the furnace and is in the hot zone. Heating is continued for 7 or 15 minutes respectively after raising the retort, i. e., 8 or 17 minutes after its insertion in the furnace. The progress of gasification is followed by reading the volume of gas collected in the eudiometer, the levels being kept as even as possible. Volumes of gas are noted at intervals of 30 seconds.

Tests at  $900^{\circ}$ C. are completed after 7 minutes, those at  $600^{\circ}$ C. after 15 minutes, reckoned from the time of raising the retort into the hot zone. Gasification never ceases entirely, since there is always a slight reflux of the tar condensed in the upper part of the retort tube which is gasified by 'cracking'.

After 7 or 15 minutes respectively, the retort tube is lifted out of the furnace and left connected with the eudiometer in a place free from draughts until the gas has acquired room temp. at which the final volume is read.

It will be found useful to plot curves from the minute observations. These cannot be reduced to N. T. P. but will show the general progress of gasification. After cooling, the retort tube and scrubber-condenser are disconnected from the eudiometer. The

piston is lifted from the retort with a hook. The coke residue is then turned out from the retort and weighed. The retort tube is then weighed in order to obtain the weight of tar in it. This may include a little carbon, but as this is produced by the cracking of primary carbonisation products, the error introduced is negligible.

The condenser containing liquor and the bulk of the tar is weighed. The liquor is then estimated by drying the condenser for 30 minutes at  $100^{\circ}\text{C}.$ ; on adding the weight of tar found on re-weighing the condenser to the weight of tar in the retort, a value for total tar is obtained.

The standard apparatus having nichrome wire wound furnace should not be used above  $950^{\circ}\text{C}.$  Temperatures up to  $1300^{\circ}\text{C}.$  can be obtained if platinum resistance wire is employed.

### EXPERIMENT 88.

#### **Analysis of the Laboratory Bench-gas. Hempel's Method.**

##### **General Remarks :—**

We owe to Bunsen and his pupils the methods of gas analysis practised to this day. It is on record that his services were requisitioned by Sir Lowthian Bell when he wanted to draw up a heat balance sheet for the Iron Blast Furnace, for which purpose the analysis of the gas from it was necessary.

The first thing to note in connection with gas analysis is that the percentages by volume, not by weight, of the constituent gases are determined. On account of the great changes taking place in the volume of a gas with changes of temperature and pressure, care has to be taken to maintain these the same throughout an experiment.

Secondly on account of the solubility of gases in liquids over which they have necessarily to be confined in making an analysis, an endeavour should be made to use only those in which they are least soluble or to saturate them with the gases to be examined and use the liquids so saturated as the confining liquids.

Thirdly, the connecting tubes between the measuring burette and the pipettes containing the absorption reagents must be of short lengths of capillary glass tubing. The rubber tubing used for connecting the glass parts should be such that the gases to be examined do not come into contact with it, that is to say, the glass parts connected by rubber tubing should come into contact with each other.

Fourthly, on account of the liability to leakages taking place when transferring gases from the measuring burette to the absorption pipette and vice versa, the pieces of rubber tubing slipped on to glass tubing should be held tightly in position by means of short rubber bands or ligatures. No special bands or ligatures are required.  $\frac{1}{8}$  inch length pieces may be cut from the rubber tubing which is slipped on and used as bands. Two or three such bands will do for each connection. Such bands are particularly required in the 'explosion' method of analysis.

The Bench-gas in use in many of the Laboratories in this country is derived from the cracking, at about 800°C, of an inferior grade of kerosene oil. Some Laboratories are supplied with the gas undiluted with air whereas others are supplied with the gas after dilution with about 50% by volume of air. The method described below is applicable both to the undiluted and the diluted gas supply.

The constituents present in the undiluted gas are  $C_nH_{2n}$ ,  $CH_4$ ,  $C_2H_6$ , and  $H_2$ . In the diluted gas, oxygen and nitrogen are present in addition.

It may be pointed out here that no endeavour is made to separately determine ethylene, propylene, etc. gases which are the members of an unsaturated hydrocarbon group. Nor is any attempt made to determine separately methane and ethane. It is sufficient for all practical purposes to determine the % of the members of the saturated and unsaturated groups.

The properties made use of are the solubilities of the constituent gases in certain media. Where no solvents are known, the method adopted is combustion followed by absorption of the carbon di-oxide formed, in a solution of caustic soda or potash. The combustion is either rapid or slow. The rapid combustion method is often spoken of as 'explosion' method. On account of the high pressures developed momentarily and on account of the high solubility of  $CO_2$  in water with increase of pressure, the explosion method necessitates the use of mercury as the confining liquid.

The gases met with in metallurgical industries are the iron blast furnace gas, the coke oven gas, the producer gas and the roast gases from the reverberatory smelting of copper, zinc, etc. ores. The principles governing the analysis of the first three of these are the same as those governing the analysis of the Bench-gas. The chief constituent of importance in the roast gases is  $SO_2$ . A method for the determination of this is described in Expt. 91 b.

The manipulation of the apparatus for the analysis of the Bench gas is illustrative of the manipulation of the apparatus for the analysis of the gases mentioned above.

A sketch of the Hempel burette and the different types of absorption bulbs is given in figs. 34a-34g. A sketch of the device used for drawing a sample of this gas is also given. The bench gas issues at a pres-

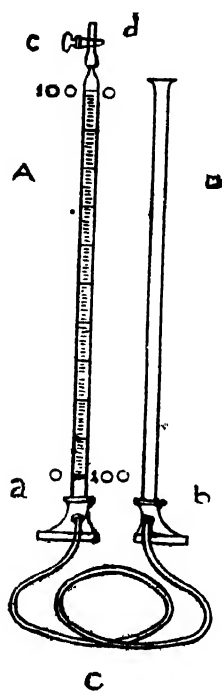


Fig. 34 a.

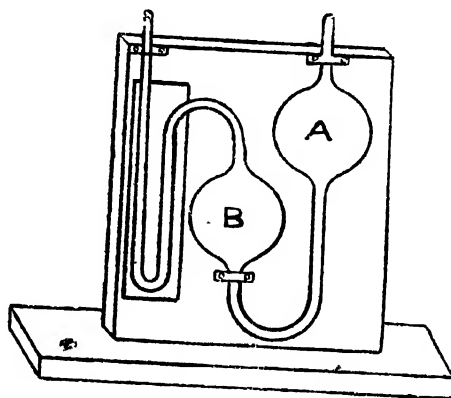


Fig. 34 b<sub>1</sub>.

sure higher than that of the atmosphere and the pressure is expressed in inches of water. Connect the end P of the sampling bottle to the gas pipe by means of a piece of rubber tubing. Expel the air in S by raising the levelling bottle which is filled with water and by keeping the pinch clamp P<sub>2</sub> open. When S is full of water release the clamp P<sub>2</sub>, open P<sub>1</sub> and the gas tap. Lower L. The gas enters and fills the bottle S. As this gas is mixed with a small volume of the air in the rubber connecting tubes, this is expelled from S by raising L and opening the clamp P<sub>2</sub>. When all the gas in S is



expelled and water is coming out of E, close  $P_2$  and open  $P_1$  and the gas tap. Lower L at the same time. By this means a sample of the Bench gas, unmixed with air from the connecting rubber tubes, is obtained. A simpler method is to allow the Bench-gas to stream through the connecting rubber tube for 2-3 minutes and then to collect the sample in S as above described.

**Transfer of gas to the Hempel burette:—**

The next operation consists in transferring a portion of this gas to the Hempel burette. To do this, first fill the burette and connecting capillary tube with water by raising the levelling tube and opening the cock C so as to communicate with the atmosphere. Next connect the capillary end E of the bottle S with the free end of the burette by a short piece of tubing. Open  $P_2$ , raise L, and lower the levelling tube. When about 100 ml. of gas have collected in the burette, close  $P_2$  and the stop-cock 'C' of the burette and disconnect the end E.

The volume of gas in the burette is to be measured by bringing the two tubes together so that the levels of water in them are the same. In a test, the burette read 99.6 ml. at the Laboratory pressure and temperature. The next operation consists in passing the gas into a number of absorption pipettes one after another in a definite order. The order in which they are to be used is the following :—

1. Caustic Potash pipette.
2. Fuming sulphuric acid pipette followed by KOH pipette.
3. Alkaline potassium pyrogallate pipette.
4. Ammoniacal cuprous chloride pipette.

In the first of these  $\text{CO}_2$  is absorbed, in the second

unsaturated hydrocarbons of the formula  $C_nH_{2n}$  are absorbed, in the third oxygen, and in the fourth carbon monoxide. After the absorption of these constituents there will remain, hydrogen, hydrocarbons of the methane series, mostly methane, and nitrogen. As already pointed out, there is no absorbent known for the two first; they are estimated by explosion with excess air or oxygen whereby hydrogen is burnt to water and methane to  $CO_2$  and  $H_2O$ . An observation of the volume before and after explosion combined with a measurement of the volume of  $CO_2$  by absorption in KOH pipette enables one to calculate the volumes of hydrogen and methane separately. Nitrogen, if any, is obtained by difference. The reagents for charging the different pipettes with, must be prepared and preserved with care.

#### **Caustic Potash solution :—**

Dissolve about 100 gms. of the sticks in 200 ml. of water. Keep in a bottle and close with a paraffined cork. Fill a simple pipette with the solution. 1 ml. of the solution absorbs 40 ml. of  $CO_2$ .

#### **Alkaline Potassium pyrogallate solution :—**

This is made as and when required. Dissolve 50 gms. of electrolytic KOH in 100 ml. of water. Add to the solution 15 gms. of pyrogalllic acid dissolved in 30 ml. of water, mix and immediately charge into a double absorption pipette. 1 ml. of this solution absorbs 10 ml. of oxygen.

#### **Ammoniacal Cuprous Chloride :—**

Dissolve 250 gms. of  $NH_4Cl$  and 200 gms. of cuprous chloride in 750 ml. of water. To 100 ml. of this solution add 35 ml. of  $NH_4OH$  of s.g. 0.90 and charge the double pipette with the ammoniacal solution. Keep a bundle of copper wire immersed in the mixture of ammonium cuprous chloride solution.

to prevent the solution from passing into the cupric state. 1 ml. of this solution will absorb 16 ml. of carbon monoxide.

**Filling of the pipettes with the reagents :—**

The simple pipettes (Figs. 34b<sub>1</sub> and 34b<sub>2</sub>) are easily filled. Pour through a small funnel placed in the wider tube of the pipette, the solution of caustic potash until the bulb B is full and about  $\frac{1}{2}$ " layer is present in the other bulb (A) If necessary, hasten the filling operation by sucking at the capillary end. The pipette to contain

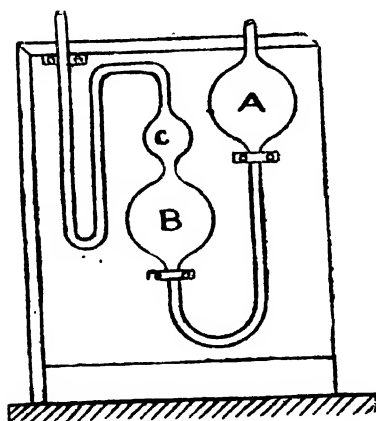


Fig. 34 b<sub>1</sub>.

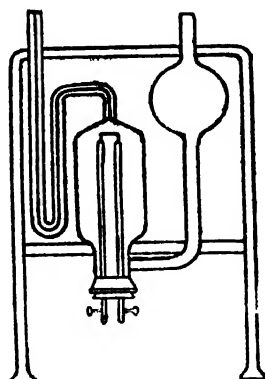


Fig 34 g.

the fuming sulphuric acid must be perfectly dry. Pour through a small funnel placed in the wider tube until the small bulb (C) with the glass tubes is full and the bulb (A) contains about  $\frac{1}{2}$  inch layer of the acid. Plug the capillary end with a short glass rod and cover the other end with a short tube closed at one end. The glass tubes serve to increase the area of contact.

**To fill the double pipette with potassium pyrogallate :**

Fill the pipette ( Fig. 34c. ) with hydrogen from a Kipp's apparatus. Connect the capillary end by means of 20 inch long india-rubber tubing. Dip this tube into the potassium pyrogallate solution contained in a 200ml. measuring cylinder. Suck at the wider end W for a minute. Raise the measuring cylinder about 20 inch above the working table and hold in this position until the bulb R is full and there is about  $\frac{1}{2}$  inch layer in the bulb S next to it. Drive the liquid in R by blowing through the mouth at the capillary end, to S

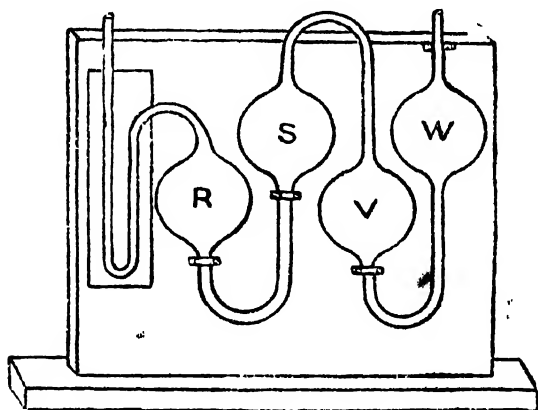


Fig. 34 c.

so that this is almost full. Keep the capillary end closed by a pinch clamp. Pour about 100 ml. of water into the bulb W. Release the clamp. The water in W works back into V and some (20 ml.) is left in W. At the same time the reagent in S works back into R and fills it. The water in V and W serves as a seal, prevents the reagent from coming into contact with air each time it is used, and thus prevents it from weakening unnecessarily. A better way of charging the double

pipette with pyrogallate solution is first to introduce the caustic potash solution from a burette, the jet being connected by rubber tubing to the capillary end of the pipette and then the pyrogallic acid solution (about 15 gms. in 30 ml. of water). The two solutions mix in the pipette and the reagent is not weakened by exposure to air during the filling. Bulbs V and W are charged with water as before.

**Ammoniacal cuprous chloride reagent :—**

The filling of the double pipette with this reagent is done in exactly the same manner as in the case of the pyrogallate pipette.

Special emphasis is laid on the order of absorption because pyrogallate absorbs both oxygen and  $\text{CO}_2$ , and ammoniacal cuprous chloride absorbs  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_4$ , and CO. The reactions that take place during the absorption are, excepting in the case of  $\text{CO}_2$ , which yields  $\text{K}_2\text{CO}_3$  with KOH, complex. In the case of the absorption of oxygen by potassium pyrogallate, potassium acetate and formate are among the products. In the case of CO, the unstable compound  $\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO}$  is formed. In the case of fuming sulphuric acid, a compound of ethylene with the acid is formed. It has the formula  $\text{C}_2\text{H}_6\text{S}_2\text{O}_7$  and is known as ethionic acid.

**Procedure :—**

Connect the Hempel burette containing 99.6 ml. of the Bench gas, with the capillary end of the KOH-pipette by means of a short piece of rubber tubing. Make a mental note of the position of the KOH solution in the capillary tube. Drive the gas over into the pipette by raising the levelling tube. When completely transferred, shake the pipette so that the liquid comes into intimate contact with the gas. Let it stand for two

or three minutes. Slowly lower the levelling tube so that the gas passes into the burette. When KOH solution stands at the original level in the capillary tube, close the cock of the burette, adjust the levels and note the reading. Repeat passing into the pipette and repassing to the burette until the reading is constant on adjusting the levels.

Pass next into the fuming  $\text{H}_2\text{SO}_4$  pipette. ( See Fig. 34b<sub>2</sub>. ) Use a dry capillary tube to connect the burette with the absorption pipette. Pass and repass ( 3 or 4 times ). Due to the presence of fumes of the acid and the consequent high vapour tension, the reading must not be taken straight. Remove these fumes by absorption in KOH solution pipette, adjust the levels and then note the reading. Repeat the operations until the reading is constant.

Adopt the same procedure in turn with the pyrogallate and the ammoniacal cuprous chloride pipettes.

**Example :—**

Volume of gas taken	=99.6 ml.
After removal of $\text{CO}_2$	=99.6 ml.
After removal of $\text{CO}_2$ by repassing	=99.6 ml.
Hence % of $\text{CO}_2$	= nil
After removal of $\text{C}_n\text{H}_{2n}$ with fuming $\text{H}_2\text{SO}_4$ (and KOH)	} = 81.4 ml.
After repetition	
Hence % of $\text{C}_n\text{H}_{2n}$	= 18.2 ml.
After removal of oxygen by absorption in pyrogallate	} = 70.2 ml.
After repeating	
Hence % of oxygen	= 11.2
After removal of CO	= 70.2 ml.
After repetition	= 70.2 ml.
Hence % of CO	= nil.

### Procedure for the determination of $H_2$ and $CH_4$ :-

Transfer a portion of the residual gas to a large size explosion pipette ( Fig. 34e ) filled with mercury. A convenient volume is about 12ml. The remainder of the gas is confined in the pyrogallate pipette to draw upon in case the test fails to explode or an accident happens. Admit an exactly measured volume of air (about 55 ml.) into the mercury pipette. Pass the mixture into the burette and repass into the pipette so that the gases

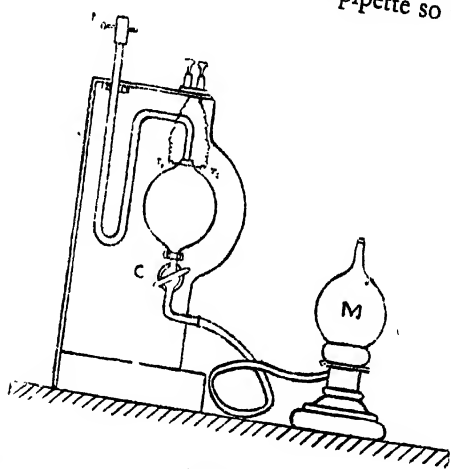


Fig. 34e.

are well mixed. Admit a few drops of water from the burette into the pipette. Close the pinch clamp T. Disconnect the burette. Insert a short piece of glass rod into the rubber tube near the pinch clamp T. Reduce the pressure somewhat by lowering the leveling bulb. Close the stop cock C. Pass sparks from an induction coil the secondary terminals of which are connected by insulated leads to  $t_1$  and to  $t_2$  and the primary terminals connected to the poles of a single storage cell. The loudness of the report is a measure of the vigour of the oxidation of  $H_2$  and  $CH_4$ . In case

no report is heard, the test will have to be repeated using a different proportion of air. After the explosion, transfer the gases to the burette by slowly raising the reservoir M after opening the stop-cock C. Measure the volume of the gases left after the explosion. Pass into the KOH pipette and obtain the volume of  $\text{CO}_2$  present in the residual gas after explosion. The following example will make the calculation clear.

Volume of gas taken for explosion, after the absorption of $\text{CO}_2$ , $\text{C}_n\text{H}_{2n}$ , $\text{O}_2$ , $\text{CO}$ is	12.6 ml.
Volume of air admitted for explosion	55.4 ml.
Total volume before explosion	68.0 ml.
Volume of products after explosion	59.0 ml.
Total contraction	9.0 ml.
Volume after absorption in KOH pipette	55.0 ml.
Volume of $\text{CO}_2$	4.0 ml.

From the equation,  $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ , it is clear that 4 ml. of  $\text{CO}_2$  must have resulted from 4 ml. of  $\text{CH}_4$ . It is also clear that the contraction in volume due to  $\text{CH}_4$  explosion is twice its volume. It must be remembered that the steam is condensed to the liquid state and that the volume occupied by the water so formed is negligible. Hence, of the total contraction of 9 ml., a contraction of 8 ml. is accounted for by the combustion of 4 ml. of  $\text{CH}_4$ . 1 ml. contraction is due to the combustion of  $\text{H}_2$ . From the equation  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ , (2 volumes of hydrogen plus 1 volume of oxygen yielding water, the volume of which is negligible,) it is clear that whenever 3 volumes disappear producing  $\text{H}_2\text{O}$ , there must be 2 volumes of  $\text{H}_2$  present. Volume of  $\text{H}_2$  present in the 12.6 ml. of gas taken for explosion =  $1 \times \frac{2}{3}$  or 0.7 ml.



12.6 ml. contain 0.7 ml. of  $H_2$  and 4 ml. of  $CH_4$

70.2 „ „ 0.7×70.2/12.6 of  $H_2$  and

4×70.2/12.6 of  $CH_4$

99.6 ml. of the gas taken for analysis contain

.7×70.2/12.6 ml. of  $H_2$  and 4×70.2/12.6 ml. of  $CH_4$ .

100 ml. of the gas will contain .7×70.2×100/12.6 99.6

ml. of  $H_2$  and 4×70.2×100/12.6×99.6 ml. of  $CH_4$

Therefore, %  $H_2$  is 3.91 and %  $CH_4$  is 22.38.

The composition of the Bench gas then is as follows :— $CO_2$  Nil.  $C_nH_{2n}$  18.2%,  $O_2$  11.2%,  $CO$  Nil,  $CH_4$  22.4%,  $H_2$  3.9%, and  $N_2$  44.3% ( by difference ).

The presence of oxygen and nitrogen in the Bench-gas is due to the intentional admixture of the gas with air, before the distribution of the gas to the laboratories. The object of admixture with air is to decrease the heating value of the gas. Pure oil gas will be a very rich gas having a high calorific power and will contain about 50% of  $CH_4$ , 42%  $C_nH_{2n}$ , and about 8%  $H_2$

NOTES :—

(1) Bromine water may take the place of fuming sulphuric acid for the absorption of unsaturated hydrocarbons. The use of this reagent is attended with no risk of fracture of the pipette, which results from inadvertently admitting drops of water into the pipette, charged with fuming sulphuric acid. When using this reagent, it is also necessary to absorb the bromine vapours by passing through KOH pipette and then to take the reading. 1% bromine is best suited for the purpose and is made by diluting one volume of saturated bromine water with two volumes of water. The compound formed with ethylene has the formula  $C_2H_4Br_2$ . This is an oily liquid.

( 2 ) Oxygen in place of air is also used for the explosion of a fractional volume of the gas left after absorption of  $\text{CO}_2$ ,  $\text{C}_n\text{H}_{2n}$ ,  $\text{O}_2$ ,  $\text{CO}$ . In either case it is necessary to calculate the volume that is to be used. When too large an excess is used, the explosion may take place without violence but the results will be inaccurate; when too small a volume is used, no explosion and therefore no oxidation of  $\text{CH}_4$  and  $\text{H}_2$  will occur. The proper proportioning of the mixture to be exploded presupposes a knowledge of the composition of the gas. According to Bunsen, an explosion will occur and the results will be very accurate if the ratio of the volume of combustible gases to the volume of noncombustible gases is equal to  $1/4$ . This ratio holds good for hydrogen. It is different for different gases. But, as a fair approximation, it may be used in the case of a mixture of  $\text{CH}_4$  and  $\text{H}_2$ . When the nature and composition by volume of the combustible gases is not known, a series of trials is necessary using for the same volume of the gaseous mixture varying volumes of air or oxygen and exploding the mixture obtained in each case. When an explosion does occur with a particular mixture, the volumes of  $\text{CH}_4$  and  $\text{H}_2$  are calculated. Assuming the values for  $\text{CH}_4$  and  $\text{H}_2$ , the volume of air or oxygen to satisfy the above requirement is calculated and the test repeated. The values thus obtained for  $\text{CH}_4$  and  $\text{H}_2$  are more accurate than those obtained with a mixture not properly proportioned before the explosion.

Instead of trying with varying proportions of air or oxygen to explode the gaseous mixture to be analysed, it is advantageous to explode a mixture by the introduction of about 10-15 ml. of electrolytic gas into the explosion pipette. This gas is obtained by the decom-

position of a 5% solution of barium hydroxide in distilled water. The gas thus obtained is purer than the gas obtained by the electrolysis of water acidulated with sulphuric acid. A convenient form of apparatus for the generation of the gas is illustrated in Fig. 34 i. The electrodes, which may consist of two heavy platinum wires are partly covered with a shield of glass tubing and inserted through a rubber stopper at A. The collecting chamber B is then completely filled with the electrolyte. The current is drawn from the 220 Volt D.C. line, with a 50 watt-lamp in series with the generator. When a few ml. of the gas have collected, the air in D is put under pressure, the stop-cock at C is opened and the gas discarded because the different solubilities of hydrogen and oxygen in the solution slightly affect the proportions. Thereafter, the pipette may be used both for generat-

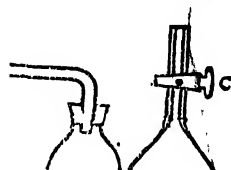


Fig. 34 i

ing and storing the gases. The current should be regulated to give about one litre per hour.

It must be borne in mind that the electrolytic gas only helps the union of  $H_2$  and  $CH_4$  with oxygen or air. One or the other supporter of combustion must therefore be present in quantity sufficient for combination with  $H_2$  and  $CH_4$ , before introducing the electrolytic gas. This gas is introduced directly into the explosion pipette from the generator. It is not necessary to measure the volume of the gas introduced.

(3) Due to the limited capacity of the mercury explosion pipette, and also of the burette, the standard

capacity of which is only 100 ml., it is not possible to use the entire volume of the residual gas for explosion, though such a procedure will lead to more accurate results, but, for the reason mentioned, only a fractional volume is used. For example, about 280 ml. of oxygen will be required for the explosion of the 70.2 ml. of the gas left after removal of  $\text{CO}_2$ ,  $\text{C}_2\text{H}_{2n}$ ,  $\text{O}_2$ ,  $\text{CO}$ . This large volume cannot be accommodated in the explosion pipette which does not exceed 250 ml. capacity.

(4) The few drops of water run into the pipette after transferring the mixture to be exploded, act as catalytic agent and promote the explosion. Perfectly dry  $\text{H}_2$  and  $\text{O}_2$  will not explode.

(5) The products after the explosion consisting of  $\text{CO}_2$ ,  $\text{N}_2$ , and surplus oxygen may be measured over water, without fear of dissolving any of the  $\text{CO}_2$ .

(6) The explosion should not be conducted in a pipette containing water in place of mercury because just at the moment of explosion very high pressure is produced and the  $\text{CO}_2$  formed will then go into solution and the results will be vitiated thereby.

(7) The estimation of hydrogen may be separately made by passing the properly proportioned mixture of gas and oxygen over palladium wire about 1 inch long, contained in a capillary and heating the capillary by means of a spirit lamp flame. The temperature must not run over  $300^\circ\text{C}$  as above this temperature some  $\text{CH}_4$  is likely to be burnt. A temperature of  $100^\circ\text{C}$ . is sufficient for the combustion of  $\text{H}_2$ . By way of check on the explosion method of the mixed gases, the following results were obtained :—

Volume of residual gas after removal of  $\text{CO}_2$ ,  $\text{C}_2\text{H}_{2n}$ ,  $\text{O}_2$ ,  $\text{CO}$  12.5 ml.

Volume of gas with air	69.0 „
Volume after repeatedly passing over heated Pd wire	67.0 „
Contraction	1.0 „
Volume of H <sub>2</sub>	0.66 „
Perecentage of Hydrogen	3.7

In place of palladium wire, palladiumized asbestos is used by some analysts for the estimation of hydrogen. This is prepared as follows:—one gram of palladium is dissolved in a 50 ml. tall form beaker with 5 ml. HCl and 2 ml. conc. HNO<sub>3</sub>. The solution is evaporated to dryness at a temperature not exceeding 100°C. The palladium chloride formed is dissolved in 5-8 ml. of water, 4 ml. of a cold saturated solution of sodium formate are added and the mixture is then made strongly alkaline by the addition of sodium carbonate solution. One gram of long soft fibre asbestos is added to the mixture which is then heated to 100-105°C. Palladium in a very finely divided condition is deposited on the asbestos fibre. When this appears dry a little warm water is added, the fibres allowed to soak for 30 minutes and then they are filtered off through a perforated porcelain cone fitted to a funnel or through a gooch crucible. The fibres are washed free of sodium salts, using water. They are then dried and preserved in a stoppered bottle. The fibre is introduced into a 1 mm. bore capillary tube which is about 12 inches long. It is then pushed into the middle part of the capillary. This is then bent into a tube of the form shown in Fig. 34h, the bottom bend containing the palladiumised asbestos and the two right-angled bends serving as points of suspension when an experiment is made. A water-bath surrounds the U tube containing

the catalyst and is maintained between 80 and 90°C. Under these conditions the fractional combustion of hydrogen only is effected. The rate of passing the gas should be such that there is no visible glow of the catalyst. A desirable rate is 15 ml. of the gaseous mixture per minute. It must be remembered that the hydrogen is burnt to water in the presence of the catalyst and that it is not a case of mere occlusion of the hydrogen gas. Therefore sufficient air or oxygen must be mixed with the gas prior to passage over the catalyst.

Methane can also be estimated by passing it after admixture with air or oxygen over the palladiumized asbestos catalyst. As the temperature at which the combustion takes place completely is of the order of 700°C., the catalyst must be contained in a silica tube, of very small bore, about 1 mm, i. e. of the type used for thermo-couple elements in Pyrometry Experiments. It should be about 9-10 inches. long. The catalyst should be pushed into the middle part of the tube and should occupy about 1-2 cms. in length. It should be loose enough to admit of the passage of gas. Only the portion of the tube containing the catalyst should be heated by the Bunsen burner to about 700°C.

In using the palladium wire or the palladiumized asbestos, an absorption pipette filled with water serves for passing the gaseous mixture to and from the gas-measuring burette.

The step-wise determination of hydrogen and methane has the advantage that accidents inherent in the explosion method are avoided.

**The Slow Combustion Method :—**

(8) Yet another alternative to the step-wise deter-

mination of hydrogen and methane is the slow combustion method. This is carried out over water contained in a pipette of the type shown in Fig. 34 d. A two-holed cork fits the bottom of the cylindrical bulb. Through each hole passes a glass tube about 15 cms. long and about 3 mm. internal diameter. Platinum wire (No. 28 gauge) is fused on to one end of each. The ends of the wires to go into the cylindrical bulb are connected by a spiral of platinum wire about 4-5 cms. long. The free ends of the platinum wire are connected by copper leads to a 220 Volt supply line through a lamp-resistance board with an ammeter in circuit to indicate the current passing through the platinum wire. The current should be adjusted to such strength that the platinum spiral will be at a yellow heat. A measured volume of oxygen is introduced into the bulb sufficient for the combustion of  $H_2$  and  $CH_4$ . The gas to be analysed is then very slowly led from the Hempel burette into the cylindrical bulb and then taken back into the burette. The further steps in the process and the method of calculation are the same as those already indicated for the explosion method, namely, the reading of the volume after the combustion, and the measurement of the volume of carbon dioxide formed by absorption in the caustic potash bulb.

(9) In place of potassium pyrogallate for the absorption of oxygen phosphorus may be used. The objection to the use of this arises from the fact that traces of impurities have a poisoning effect and the oxygen is not absorbed. Also, the filling of the pipette with this reagent is tedious and requires great care. When it is a question of estimating oxygen only in a sample of air, the phosphorus pipette may be used. The objection to the use of it on the score that it is very slow





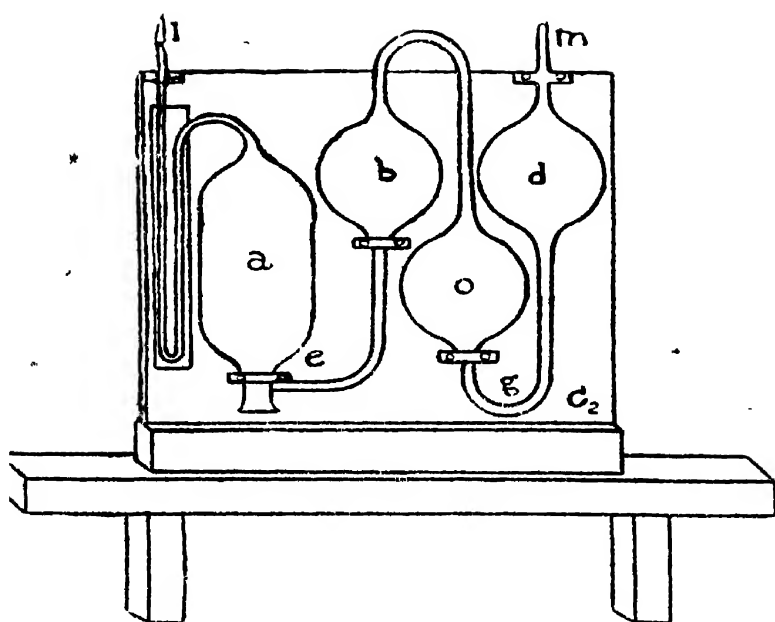


Fig 34d. To face p. 509

in action at temperatures below  $15^{\circ}\text{C}$ . is without force in this country. The following is the procedure for filling the pipette with phosphorus:—In a tall form 400 ml. beaker, containing about 200 ml. water, introduce yellow phosphorus so that it is completely under water. Heat the beaker over a mush room top burner so that the phosphorus melts to a liquid. Dip a piece of glass tubing about 15 cms. long and 3 mm. bore, open at both ends into the molten liquid. Close the open end with the fore-finger, lift the tube from the beaker and plunge into a beaker of cold water, with the open-end of the tube still closed. When the phosphorus has solidified, it will fall to the bottom of the beaker, If it does not fall, it may be pushed out by slight pressure using a thin glass rod, Several sticks of phosphorus thus made are withdrawn from the beaker by means of a pair of tongs and introduced into the cylindrical bulb for solid reagents, the pipette being inverted while charging it with the sticks.

( 10 ) On account of the warmth of the hands and the consequent increase in the volume of gas, the burette should be handled at its wooden base, whenever volumes are read off after adjustment of levels.

( 11 ) Caustic soda or potash purified from associated carbonate by means of alcohol is unsuitable for preparing the pyrogallate reagent as the one so made evolves  $\text{CO}$ . Electrolytically prepared  $\text{KOH}$  and  $\text{NaOH}$  do not give rise to  $\text{CO}$ . Hence they alone should be used. For absorption of  $\text{CO}_2$  however, it is immaterial which reagent is used, whether the one purified by alcohol or the one electrolytically made.

( 12 ) Ammoniacal cuprous chloride is preferred to cuprous chloride made strongly acid with  $\text{HCl}$ , as its absorbing power is greater, and as it remains in tact for a longer period. Before reading off the volume of

CO absorbed, the residual gases should be passed through a pipette containing dil. HCl. The solution which has been in use has a tendency to give up carbon monoxide to gaseous mixtures low in their CO content, which may be passed through it. The practice is therefore to use two such pipettes. The first is a solution which has been in use for some time and the second is a fresh solution.

### EXPERIMENT 89

#### Analysis of Bench-gas with the Orsat Apparatus.

##### General Remarks :—

On account of the compact nature and the consequent easy portability of the apparatus, this is widely used in Works' Laboratories. The principles governing the analysis of gases with this apparatus are the same as those with the Hempel burette and accessories, namely, absorption of one constituent after another in a certain sequence by passage through absorbents. The apparatus is shown in Fig. 35 L is a levelling bottle connected by

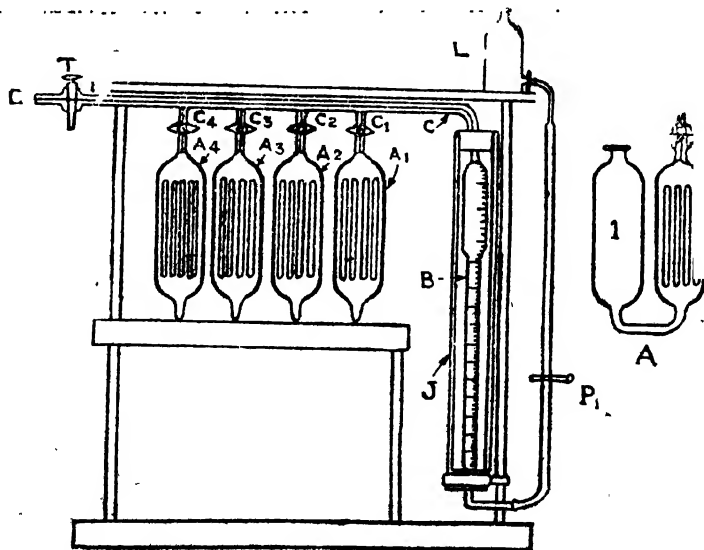


Fig. 35

means of a piece of rubber tubing about 30 inches long to a burette with two series of graduations running from 100 at the bottom to 0 at the top and vice versa. This burette is surrounded by a jacket-tube J containing cold water. The upper portion of the burette is an enlarged cylindrical bulb. This is connected by a short piece of rubber tubing to a thick capillary tubing with fused-on side tubes, and having at its end a three-way tap T. Each side tube carries a tap, and is joined by thick rubber tube with a U shaped absorption pipette. The first one nearest the burette contains KOH solution, the second bromine water, the third alkline pyrogallate, the fourth ammoniacal cuprous chloride, and the fifth water. The solutions used are of the same strength as those used when analysing with the Hempel apparatus. To cause rapid absorption, the absorption vessels contain a number of short lengths of glass tube, which when wetted with the reagent expose a large surface to the gas.

The open limb of the U tube is provided with an accurately bent thick capillary plug which prevents any free access of air. The limb of the U tube connected through the stop-cock to communicate with the burette ends in a capillary on which is etched a mark. Each pipette is filled with the proper absorbent up to this mark. This is done as follows :—

Turn the three-way tap T suitably so as to put the burette in communication with the atmosphere. Pour about 200 ml. of a 10% solution of NaCl acidulated with one ml. dil HCl 1 : 1 and coloured red by the addition of a few drops of methyl orange, into the levelling bottle L. Raise it so that the air in the burette is expelled and the liquid fills it completely. There should be at least an inch layer of water in L when the burette is

filled. The stop-cocks on the capillary with side-tubes should be so turned that no liquid runs into any of the U tubes when filling the burette. Turn three-way tap T so as to cut off the burette communicating with the atmosphere and place L on the working table. Pour KOH solution into the limb  $l_1$  of the absorption U tube  $A_1$ , after removing the capillary plug. The liquid does not rise in the limb with the etch mark to the same level as in  $l_1$ . Open then the stop cock  $c_1$ , so as to put the burette and the U tube  $A_1$  in communication with each other. The air is sucked into B and the liquid rises in the other limb. By a repetition of the process the absorbent can be made to reach the etch mark. In the same manner all the absorption vessels are filled, one by one, with the appropriate reagents. Care should be taken not to have more than an inch or so of liquid layer in each of the limbs at the back.

The fifth U tube connects with the stop-cock tube via a platinum capillary tube wrapped round with asbestos thread. This one serves for the estimation of  $H_2$  and  $CH_4$  by combustion.

It is desirable to start with 100 ml. of the sample of gas to be analysed so that calculations become simple. To do this proceed as follows :—

Fill the burette B completely with water by raising 'L'. Close the pinch cock ' $p_1$ '. Slip on the gas tap of the Laboratory Working Bench a piece of rubber tubing with a glass adapter, open the gas tap so that the air in the connecting tube is swept out and the gas to be examined fills it completely. Connect by a short piece of rubber tubing the end of the glass adapter to E, the capillary tube 'C'. Turn the three-way tap T suitably, putting B in

communication with the gas supply. Lower L and release the clamp. The gas streams in until the level of liquid in B goes below the 100 ml. mark. Now close the gas tap. Disconnect at E after turning off T so that B communicates neither with the atmosphere nor with the gas main. If the volume of gas is read when the levels of liquid in B and L are the same, it will be seen that more than 100 ml. of the sample have been drawn. Slightly compress the gas by raising L. Momentarily open the three-way cock T so that B communicates with the atmosphere. Close T. Now examine if the volume of gas is 100 ml., when the levels in B and L are the same. If more than 100 ml. of gas are still present, repeat the above operation until there is a volume of 100 ml. only. If less than 100 ml. are present, draw more of the gas sample by connecting with the bench-gas tap and repeating the operations more carefully.

Perform the following operations after 100 ml. of the gas sample have been confined in the burette :—

Open  $c_1$  and raise L slowly so that the gas passes into  $A_1$ . Lower L so that the gas passes back into B from  $A_1$ . Repeat twice. Bring the liquid (KOH) back to the original mark ( the etch mark ) and read off the volume in the burette B when the levels in B and L are the same. Pass the gas back and forth once more. Read the gas volume. If it is the same as before, all the absorbable constituent, namely  $CO_2$ , has been absorbed. Repeat the process successively with the other absorption pipettes until only  $H_2$ ,  $CH_4$  and  $N_2$  are present. At this stage, proceed as in the 'Slow Combustion Method' described in Expt. 88. That is, use a portion of the residual gas only for combustion. The rest is confined in the potassium pyrogallate pipette. Mix it with 30-40 ml. of oxygen. Heat the platinum

capillary wrapped with asbestos, with a Bunsen burner while the gaseous mixture is being passed to and fro. Passing twice or thrice will do. Transfer the products of combustion to B. Note the contraction. Pass into KOH solution and note the contraction. This last contraction gives the volume of  $\text{CO}_2$  formed and therefore the volume of  $\text{CH}_4$  originally present. For calculation of the volume of hydrogen, see Expt. 88.

NOTES :—

( 1 ) Care should be taken to see that the caustic potash solution or the pyrogallate solution does not run up to the stop-cocks. If accidentally any gets in, the stop-cock should be taken out and wiped with a piece of cloth or filter-paper soaked in dil. HCl. This should be done 3 or 4 times. Finally it is thinly smeared over with vaseline and then restored to its seat.

( 2 ) Leakages of gas occur through interchange of stop-cocks. Each cock should be returned to its appropriate seat. If leaks occur even after this precaution, a little of a mixture of emery and olive oil is applied thinly on to the stop-cock and it is then turned a number of times in its seat until a snug fit is obtained.

( 3 ) Cracking of the absorption tubes must be guarded against by interposition of an asbestos sheet when heating the platinum capillary.

#### EXPERIMENT 90.

#### Calorific value of Bench-Gas using the Junker Calorimeter.

The essential parts of the Junker gas calorimeter outfit are : (1) a pressure regulator for the supply of gas at a constant pressure to a burner, (2) a gas meter for reading the volume of gas supplied, (3) a burner of the Bunsen type in which the gas is burnt, (4) a calorimeter to absorb the heat of the products of com-

bustion of the gas under test, (5) thermometers to register the temperature of the inflowing and the outflowing water and also of the products of combustion escaping after they have given up their heat, (6) two graduated cylinders : one in which the outflowing water is collected, and a second one to collect the condensed water from the products of combustion and (7) a constant head arrangement for supplying water to the calorimeter at a constant head or pressure. The one essential difference between this calorimeter and other forms in ordinary use lies in that the former is, what is sometimes described as, the 'flowwater' calorimeter whereas the latter are 'still-water' calorimeters. In the type under description, water is made to flow through a jacket containing a number of tubes and the heat of the products of combustion passing through the tubes is taken up by the flowing water, that is water in motion. In the ordinary types, the water is 'still' or 'at rest' and the heat of the bodies placed in it is taken up by it.

Fig. 40a shows the assembled apparatus for a determination.

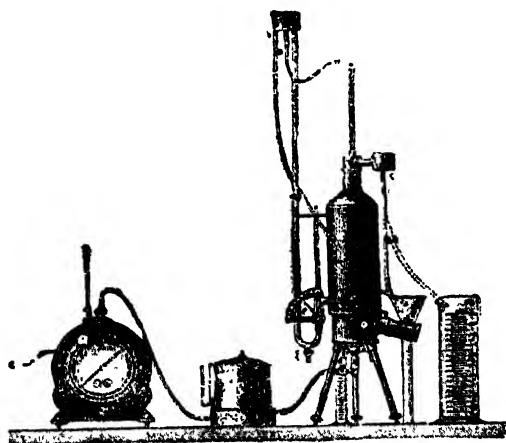


Fig. 40a.



Fig. 40b shows the Junker calorimeter in section.

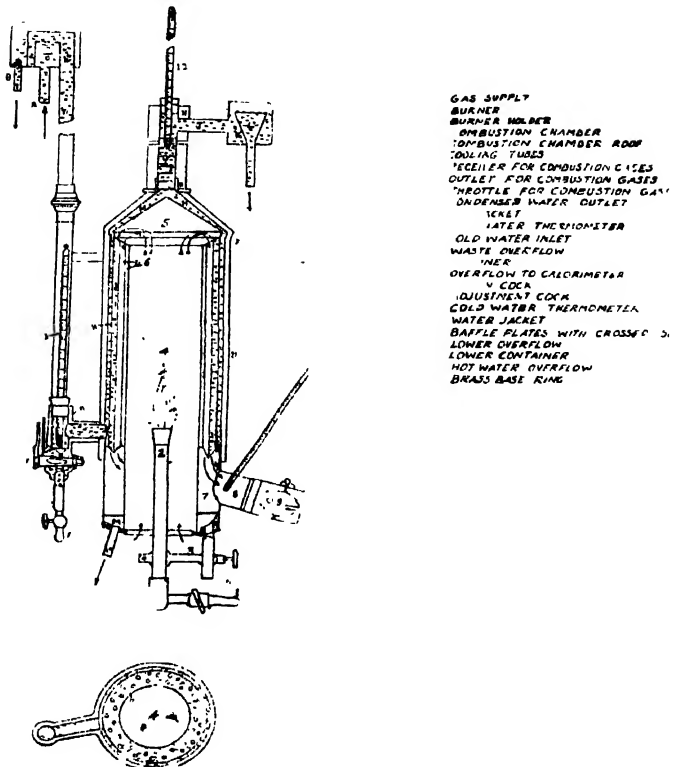


Fig. 40b.

Fig. 40 c shows the governor, i. e., the device for regulating the pressure at which gas is fed to the burner.

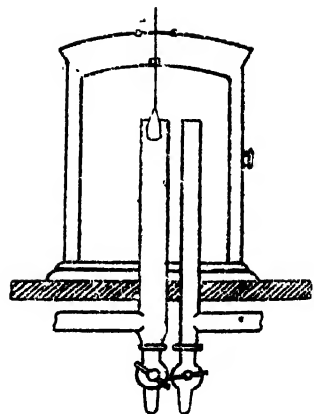


Fig. 40c.

In a run, the first step is to burn the gas in the burner so that the gas jet burns with a flame of normal height and intensity. The air-hole of the burner should be so adjusted that the gas burns silently. Any noise or roar indicates that more air than is necessary is admitted in which case the maximum heating value is not realised. The burner is next placed in a chamber free from draughts. Water under constant head is fed into the calorimeter. The quantity is regulated by a tap. When the temperature of the outflowing water has reached a steady stage, that is to say, it has become constant, the gas-meter is read and the outflowing warm water is collected in the measuring cylinder so that the volume is 1500–2000 ml. The volume of gas that has passed through in the interval necessary for collecting this volume of water is read on the gas-meter. The air for combustion enters through the long tube attached to the constant-head-water arrangement, thus ensuring the same temp. for it as for the water fed into the calorimeter. The products of combustion escape through the tube placed at the side near the bottom.

The following observations were made in an experiment :—

Volume of gas used 0·1 cubic foot.

Volume of water collected 2 litres.

Temperature of inflow-water 23·6°C.

Temperature of outflow-water 31·9°C.

Hence, the quantity of heat on burning 1 cubic foot of the gas is equal to  $\frac{2 \times 8 \cdot 3}{0 \cdot 1}$  or 166 kilogram calories, (i. e.)  $166 \times 3 \cdot 968$  or 650 B. Th. units.

1 Kilogram = 2·205 lbs. = weight of 1 litre of water.  
1° C. = 1·8 F. Hence 1 kilogram calorie =  $3 \cdot 968 \cdot \text{B. Th. U.}$

The value thus obtained is the gross heating value. In actual practice, steam which is one of the products of combustion escapes through the chimney and is not condensed. But in the experiment the steam is condensed and its heat taken up by the flowing water of the calorimeter. A deduction should be made for the amount of heat thus absorbed. This amount can be obtained by collecting any water that may drop from the tubes through which the products of combustion make their exit.

The volume of water collected during the run was nil. This is partly because the gas is not rich in hydrogen and partly because the volume of gas burnt is only 0.1 c. ft. That this must be so can be seen by a simple calculation from the composition of the gas (see Experiments 88 and 89). Supposing, however 2 ml. of water are collected during a run, the quantity of heat given up by 20 ml. of water collected when 1 c. ft. of gas is burnt is  $\frac{20 \times 600}{1000}$  or 12 C. Deducting this from the gross calorific value, the net calorific value of the gas is 166-12 i. e., 154 C. 154 C.=616 B. Th. U.

NOTES :—

(1) Junker's gas calorimeter is used for the direct estimation of the heating values of industrial fuel gases. It is more often the practice to calculate their heating values from their percentage composition by volume, which is found out as shown in Experiments 88 and 89.

(2) The gas meter.—This is of the wet type. It consists of a number of lightly constructed compartments disposed on a central spindle. This is caused to rotate by the individual compartments becoming filled with the gas on their passage through a water seal disposed over the inlet to the meter. Each compartment has a definite capacity, consequently a known

volume of gas is passed through the meter per revolution of the spindle. This latter is geared to counting mechanism, which records on a dial the actual volume passed. The meter should be set level by means of the adjustable feet. It is filled with water up to the horizontal mark etched on the small glass disc. When filled, the opening is closed by a tight-fitting cork. The gears must be oiled from time to time, particularly in Laboratories where the testing is carried out a number of times daily.

(3) The Governor:—This is similar in shape to gas-tanks of large size. It is of the balanced type. It consists of a bell disposed in a water seal and carrying a conical seated valve, which, by the rise or fall of the bell, opens or closes the gas inlet and thus allows more or less gas to pass according as the pressure falls or rises. The bell is balanced by weights suspended from the opposite end of the beam to that at which the bell is attached. The clearance between the cone valve and its seating in the inlet pipe can be adjusted by alteration of the weights. The addition of weight decreases the clearance and makes the governor more sensitive in its action.

A side plug is fixed in the vessel which contains the bell, the waterlevel is adjusted in this vessel by opening both inlet and outlet gas cocks to the atmosphere, water is then poured into the vessel until it flows out at the orifice for the plug, which is then placed in position.

(4) The flow of water in the calorimeter should be so adjusted that a difference of about  $10^{\circ}$  C is obtained between the cold water and the hot water. Accurate results are possible only under this condition.

(5) To prevent the formation of scales, on the tubes

through which the products of combustion pass, it is desirable to use soft water. Formation of scales will prevent the efficient transfer of heat.

## EXPERIMENT 91 a

### Flue gas Analysis :—

General Remarks—The term ‘flue-gas’ is applied to the waste gas escaping up the chimney of a boiler or a furnace, irrespective of whether they are fired by means of a solid fuel like coal or a liquid fuel or a gaseous fuel like iron blast furnace gas. Theoretical considerations show that, in the case of a boiler, fired by coal, there is no wasteful use of the fuel if the percentage of carbondioxide in the chimney gas is 14. This percentage of  $\text{CO}_2$  will mean the employment of 50% more air than is theoretically needed for the combustion of the fuel. To maintain the rate of evaporation and therefore the the power output at the proper level, this excess becomes necessary, wasteful as it is in that a part of the heat energy is carried up the chimney. But a far greater excess than 50% more air will lead to a heavier loss and the cost of power in such plants will be higher than in those restricting the air supply to what is necessary. In the case of boiler plants fired by the iron blast furnace gas, it will be enough if a 5–10% excess of air is supplied. A greater excess than this is wasteful. Knowing the composition of the gas, the composition of the flue gas is calculated for a 10% excess supply of air. The % of  $\text{CO}_2$  obtained by calculation is compared with the % of  $\text{CO}_2$  by analysis. A better control is maintained on the combustion process in the light of the figures of analysis. In recent years great attention has been paid to the economic production of power and automatic recorders of the % of  $\text{CO}_2$  in flue gas have been installed in large steam power plants.

The %  $\text{CO}_2$  in a flue gas is obtained by the use of the Orsat apparatus. On account of the great variation in the composition of the gas according as a sample of it is drawn from the middle of the chimney or from points close to the wall of the chimney where the velocity of flow of gas is much less than what it is at points far removed from it, attention must be paid to drawing a representative sample of the gas. Fig. 36d shows the arrangement for drawing a sample of the gas. This consists of a steel tube one inch in

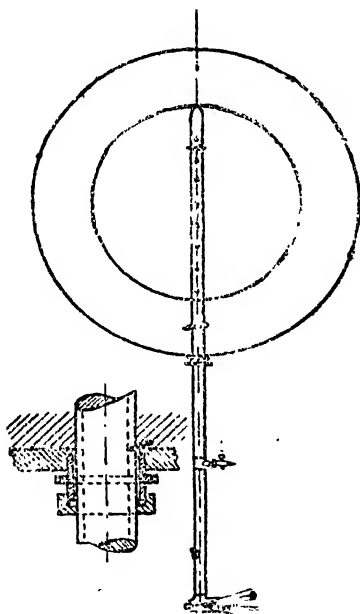


Fig. 36d

diameter, with one end closed. Holes  $\frac{1}{16}$  inch in diameter are drilled about 6 inch apart along two lines lying diametrically opposite each other, those along one line being located so as to fall opposite a point midway between two holes in the other line. The sampling tube should be long enough to extend

entirely across the gas stream, the number and size of the holes should be so regulated that their combined area does not exceed three fourths of the cross sectional area of the opening in the tube itself. For temperatures of flue gases higher than  $400^{\circ}\text{C}$ , the sampling tube should be made of silica or clay as soot in the gas stream reacts at those temperatures with iron oxide in the tube. This is connected to an aspirator. This should be operated so that the pressure in the sample tube is slightly less than that in the gas main.

The sampling pipette (Fig. 36b) of about 150 ml. capacity is connected to the pet-cock after filling it with water. It is filled with water by dipping one end of it into a beaker of water, opening the cocks  $C_1$  and  $C_2$  and sucking at the end near  $C_2$  until the pipette is full.  $C_1$  and  $C_2$  are then closed. When the aspirator has worked for 5 to 10 minutes and the air in the sampling tube has been expelled, open the cocks of the sampling pipette and collect about 120-130 ml. of the sample. Close the cocks  $C_1$  and  $C_2$  and carry the sample to the Laboratory. Raise L, the levelling bottle of the Orsat apparatus, and open T so that the burette B is filled with water. Close the pinch-clamp  $p_1$ . Connect the sampling pipette to E by means of a short piece of rubber tubing. Support a beaker of water suitably so that the cock  $C_1$  of the sampling pipette is 2 inches below the level of water in the beaker. Open  $C_1$  and  $C_2$ . Release the clamp  $p_1$ , lower L and draw the gas sample from the pipette to B.



Fig. 36b.

Close  $C_1$  and  $C_2$  when a little more than about 100 ml. of the sample have been drawn into B. Turn T so that B does not communicate either with the atmosphere or the sampling pipette. Slightly compress the gas in B by raising L so that in B the liquid level stands at the 100 ml. mark. Momentarily open T to the atmosphere so that a small amount of the compressed gas is expelled. Read off the volume when the levels in B and L are the same. If the volume of gas is not exactly 100 ml., repeat the above operations of compression and expulsion of gas until exactly 100 ml. are confined.

Instead of drawing the sample of gas from the sampling tube to the pipette and then transferring it to the burette, the apparatus may be carried to the point at which the gas sample is to be drawn and a rubber suction pump used to draw a sample directly into the burette. Fig. 36c shows a pump. It has two valves  $V_1$  and  $V_2$  working in reverse directions. When the bulb is pressed, the valve  $V_2$  operates and the air in the bulb is expelled into the atmosphere via the tap

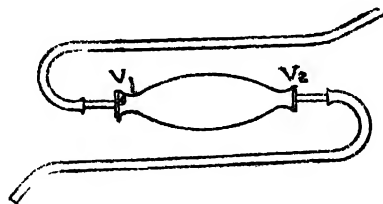


Fig. 36c.

T, which is suitably turned for the purpose. When the bulb is released, the valve  $V_1$  operates and a sample of the gas fills it. After working the pump a few times, a sample of the gas is drawn into B by turning T so as put the gas-source in communication with B.



Analyse the gas for  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{CO}$  and  $\text{H}_2$  in the manner explained in Expt. 89.

**NOTES :—**

(1) The presence of  $\text{CO}$  indicates too thick a fuel bed. Heat losses occur through  $\text{CO}$  passing through the chimney.

(2) The presence of  $\text{H}_2$  also indicates the incomplete utilisation of the heat energy of coal.

### EXPERIMENT 91b.

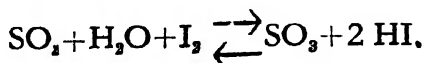
Determination of %  $\text{SO}_2$  in the flue gases from roasting furnaces.

**Object :—**

The roasting of a sulphide ore proceeds very effectively when the %  $\text{SO}_2$  by volume is about 8. When a greater volume of air than is needed to yield 8%  $\text{SO}_2$  is admitted, the hearth cools off while with less, the roasting proceeds rather slowly. As a means of control on the process of roasting, this estimation is very helpful.

**Principle :—**

When  $\text{SO}_2$  is passed into a standard solution of iodine, the following reversible reaction takes place:—



To carry to completion the reaction indicated by the upper arrow, a small quantity of sodium bicarbonate is added to the iodine solution, before passing the gases into it.

**Solutions required :—**

(1) Standard iodine solution.

(2) Starch solution. See Experiment 19.

**Procedure :—**

Fit up the apparatus shown in Fig. 39.

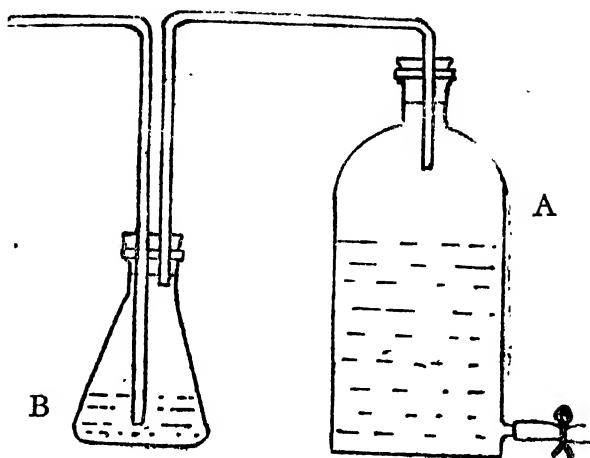


Fig. 39.

B is a wide mouthed bottle containing 10 ml. of 0.1N-iodine solution diluted with 50 ml. of water. Add to it a few drops of starch solution and about 0.5 gm. of  $\text{NaHCO}_3$ . Aspirate the gas through B by opening the pinch clamp P. Collect the water that runs out in a graduated jar, G. Shake up the iodine solution when the gases are being aspirated through it. When it is decolorised, close the pinch-clamp P. The volume of gas aspirated through equals the volume of water in G plus the volume of  $\text{SO}_2$  absorbed by the iodine solution. The temperature of the gases is that of the water in A. Titrate the excess of iodine, if any, against 0.1N- $\text{Na}_2\text{S}_2\text{O}_3$ . Assuming that all the iodine is used up, calculate as follows:—

1 ml. 0.1N Iodine = 1 ml. 0.1N-SO<sub>2</sub>.  
 = .0032 gm. SO<sub>2</sub>  
 = 1.12 ml. SO<sub>2</sub> at  
 0°C and 760 mm.

10 ml. 0.1 N—I<sub>2</sub> = 11.2 ml. at 0°C. and 760 mm.  
 = 12.3 c. c. at 30° and 750 mm.  
 (30° being the temp. of water  
 in A and 750 mm. the pressure  
 of the atmosphere at the  
 time of the experiment )

Vol. of water in G = 416 ml.

416 + 12.3, i. e., 428. ml. contain 12.3 ml. SO<sub>2</sub>  
 % SO<sub>2</sub> by volume = 2.8

#### NOTES :—

1. The method described above is known as Reich's method and is the one adopted for the determination of SO<sub>2</sub> in the gases from sulphur burners in sulphuric acid plants.

2. Automatic recorders have been installed in recent years for indicating the percentages of SO<sub>2</sub> in the gases from the roaster furnaces of copper smelting works. The Indian Copper Corporation Works at Moubhandar, Singhbhum, has such an installation.

### EXPERIMENT 92.

#### Analysis of Mine Air.

##### General Remarks :—

For the safety and the health of workers in mines, it is necessary to examine samples of mine air regularly. 3 volumes of CO<sub>2</sub> are present in 10,000 volumes of fresh air. A sample of air containing about 8% of CO<sub>2</sub> is dangerous to breathe. An increase in the CO<sub>2</sub> content of mine air may arise from one of several causes,

improper ventilation, drawing a sample of the gas immediately after explosives have been used for blasting, etc. Apart from discomfort to workers, serious accidents costing the lives of many workmen may occur through the use of naked lights in mines which are gassy, i.e., which give off marsh gas. A qualitative idea of the amounts of this gas present in a coal mine may be gained by an observation of the height of the blue cap appearing in the flame of a safety-lamp. But on account of the great variations in the capacity of observers, it is difficult to state, even approximately, the percentage of the gas in a sample of mine air. The only reliable method of examination is to make an analysis of the gas. The principles governing the analysis of a sample of mine air are the same as those already described for the analysis of Bench-gas or flue-gas. But on account of the importance attaching to the safety and the health of workers, a more exact analysis is required. The apparatus in use has been designed to contain a much smaller volume of the sample and while being of the same height as the Hempel or the Orsat burette, the diameter of the same is much smaller, making graduations to  $\frac{1}{10}$ th or  $\frac{1}{100}$ th of a ml. possible. Also, on account of the solubility of  $\text{CO}_2$  in water, mercury is generally used as the confining liquid.

On account of the importance attaching to the results of examination of a sample of mine air, it is necessary to draw samples from a number of points, from near the roof, the floor, and return airway, in separate bottles and to see to it that they do not undergo any change in transit to the laboratory where they are to be analysed.

Glass-stoppered bottles, the body and the stopper having the same numbers etched on them, free from leaks and of about 100 to 120 ml. capacity are used. The stoppers are greased with a mixture of two parts beeswax with one part of Venetian turpentine or with petroleum jelly. Leaks are detected by immersing the stoppered bottle, suitably, weighted to prevent it from tilting, in a beaker of water and heating the water. No bubbles of gas should appear, or, on cooling the water in the beaker, no water should enter the bottle.

Such a bottle should be filled with mercury and carried to the mine from which a sample is to be drawn. After pouring out the mercury into a suitable reservoir, the stopper is replaced and a rubber band put on so that the stopper is held in position. This is then sent to the Laboratory.

In the laboratory, this is inverted over a trough of mercury so that the neck is dipping into the surface of mercury. The stopper is removed, one end of a bent capillary tube is inserted into the bottle, the other end is connected by means of a short piece of thick rubber tubing to a Hempel burette filled with mercury. A sample of gas is drawn into the burette by producing negative pressure, that is, by lowering the levelling tube of the Hempel burette.

The gas so drawn is then analysed as in Expts. 88 and 89 using the apparatus described thereunder. The following is a description of the apparatus designed by Dr. J. S. Haldane for the analysis of mine air which makes it possible to obtain results correct to the second

place of decimals. The apparatus is shown in Fig 37. The burette A which is of 21 ml. capacity consists of a bulb of 15 ml. volume blown on to a narrow tube, which is graduated from 16 to 21 ml. in one-

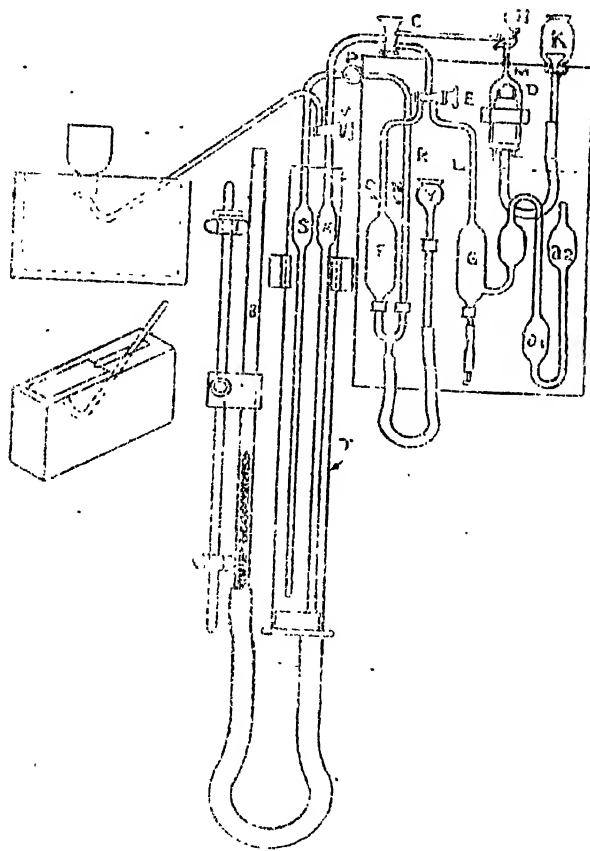


Fig. 37.

hundredths of a ml. The lower end of the burette is attached by pressure tubing to a levelling tube B. Mercury is the confining liquid used in the burette. A three-way tap V is blown on the top of the burette; one limb of this tap is connected to the absorption

bulbs through the three-way tap C, whilst the other is provided for the filling of the burette with gas sample.

The tap C communicates in one direction with the methane combustion bulb D, and its third limb connects through the tap E with either the potash bulb F or the pyrogallate bulb G.

The methane combustion bulb consists of a tube attached to the three way tap H. A mark is made on the capillary tube at M. The bottom of the bulb is closed with a three-holed rubber stopper, firmly held in place by first coating it with paraffin wax and pressing it firmly home into the bulb whilst the latter is sufficiently warm to soften the wax. Through two of the holes in the cork are passed glass tubes carrying the leads to a spiral of platinum wire. These consist of stout copper wire soldered with special solder or fused to platinum wires which in turn are fused into the top of the glass tubes. These are of such size as to give little 'play' to the copper wires. To the ends of the platinum wires, which should be about 1 inch apart, there is fixed a platinum spiral, made from 40 gauge wire. Through the third hole of the cork there is passed a straight glass tube connected by pressure tubing to the mercury reservoir K. A current of 2 amperes at a minimum of 4 volts is sufficient to heat the wire.

The pyrogallate absorption bulb G is of the usual form, having fused-on bulbs  $a_1$ ,  $a_2$ , which serve as a water-seal. The tube is filled through the lower tube, to which is attached a length of  $\frac{1}{4}$  inch diameter rubber tubing; care must be taken in filling the bulb that a sufficient volume of solution is introduced so that when it stands in the bulb at the reference mark L, the side bulb contains sufficient solution to prevent air

being drawn into the absorption bulb, and, further that the volume of water in the lower bulb effectively seals the whole bulb. The rubber tubing is closed by a long length of glass tubing, tightly fitting into the tube and wired thereto. It is advisable to keep an empty beaker below G in order to collect any solution that may leak or escape and thus prevent the damage to the surface of the working-bench.

The potash bulb which has a reference mark at O is connected to a Y tube, one limb of which is connected to the reservoir Y, the other to a capillary tube R, upon which there is a reference mark N. The top of R is connected through a three-way tap P to the 'compensator bulb' S. This bulb and the burette are immersed in the water jacket T in order to maintain a uniform temperature. For continuous or routine work, it is advisable to lead a current of cold water at the lower end of the jacket tube and to take it away from the top by means of rubber tubing attached to a glass-tube passing through a one-holed cork.

The compensator is a closed bulb of the same volume as the burette; it is for the purpose of correcting any changes in pressure and temperature that may take place in the course of an analysis. The principle adopted is to enclose therein a fixed volume of air at atmospheric pressure, and at the temperature of the water in the jacket T. The volume of the gas in the burette is always read against the pressure of the gas in the compensator, by using the potash pipette and connecting tube R as a pressure gauge. That is, the level of the potash for every reading of the burette is brought to the mark N by the reservoir Y and then by manipulation of the levelling tube B, the potash in F is adjusted to mark O, when the burette is read. ..



## NOTES :—

When putting the burette A into communication with any of the absorption bulbs, the level of mercury in B must be above that in A. This procedure will prevent the solutions being carried over or sucked into A.

**Adjustment of the Apparatus prior to an Analysis:—**

The pressure throughout the apparatus is adjusted as follows: the mercury in the burette is brought to the tap by opening V and raising B. The levelling tube B is placed in such a position that the level of the mercury is about level with the bottom of the bulb on burette A; tap V is then opened to the atmosphere and a volume of air of about 16 ml. is drawn in. When the levels of mercury in A and B are equal, V is closed. Tap H is so turned that tap C, the atmosphere and the mercury in D are in communication. Reservoir K is raised so that mercury is brought exactly to the mark M in the pipette D. Tap H is then turned so that it only communicates to tap C and the pipette D.

A slight pressure is placed on the air in A, taps V, C and E are turned to put G in communication with A, when by manipulation of the levelling tube B, the pyrogallate solution is brought to the mark L. Tap E is now closed. The tap P is turned so that connection is established between the compensator, the atmosphere and the tube R. The potash solution is adjusted to the mark N by manipulation of the reservoir Y; the tap is now turned so that communication only exists between R and the compensator. The level of the potash in F is then adjusted to mark O by manipulating the levelling tube. The level in R should then be at N.

The apparatus is now ready for use.

### Transference of sample from bottle to the burette

A capillary tubing suitably bent has one end dipping into the mercury in the trough while the other end connects by a short piece of pressure tubing with the burette top. The reservoir B is raised so that the level of the mercury therein is well above the top of the S-like bend on the burette. Tap V is placed in communication with the S bend and as the mercury reaches the top of the S bend, V is closed, then gradually opened so that the mercury flows slowly down the S, and finally a few globules overflow at the other end, a point ascertained by raising the end slightly above the level of mercury in the trough. Tap V is closed, levelling tube B is lowered so that the level therein is about the bottom of the burette.

The bottle containing the sample of gas to be analysed is inserted mouth downwards in the trough and held suitably to prevent it from tilting. The stopper is removed, the end of the S tube inserted into the bottle so as to reach nearly to the top of it. Tap V is slowly opened and a sample of gas is drawn into the burette to the 21 ml. mark, B is raised so that the levels of the mercury in B and A are approximately between the 20 and 21 ml. mark. Tap V is closed. A slight pressure is put on the gas by raising B, the tube S withdrawn from the bottle, tap V is momentarily opened to the atmosphere and then closed. A sample of gas at atmospheric pressure is thus contained in A. B is raised. the burette A is placed in communication with the potash bulb, the level in R is adjusted to N by means of the reservoir Y, and, finally, by manipulation of B the potash is brought to the mark O. The levels of

the potash solution being at O and N, the volume in A is read off by means of a lens. This is the volume taken for analysis.

**Procedure :—**

$\text{CO}_2$ —Gradually raise B passing the sample of gas into F, lower B and draw the gas back into A. Repeat this two or three times. Adjust the potash solution to the mark N in R and to O in F by manipulation of Y and B. Note the volume in A. To see if all the  $\text{CO}_2$  has been absorbed, repeat the above process. If the reading is constant, record it. Calculate % of  $\text{CO}_2$ .

$\text{CH}_4$ —Turn tap C to connect D with the burette A and to close the connection to E. Raise B to pass the gas into D. Switch on the current, with all the resistances in; cautiously cut them out until the spiral just becomes visibly red. Slightly lower B, taking care not to bring the mercury into contact with the glowing spiral. Raise B so as to pass the gas again into D. Repeat the process two or three times. Switch off the current. Allow the gases to cool. Lower B until the mercury in D is at M. Note the volume in A. Pass the gases into the potash pipette and draw back into the burette. This step carries small amounts of methane enclosed in the connecting tube to A. Pass the gases again into the combustion pipette, switch on the current, pass and repass as before, switch off the current, allow to cool and draw the gases back into the burette. Adjust the mercury in D to the mark M by manipulating B. Close C to disconnect D. Slightly compress the gas in A. Open E to connect with the potash bulb. Adjust the solution to marks N and O and then read the volume. Half of the contraction equals the volume of methane. Calculate the % of  $\text{CH}_4$ .

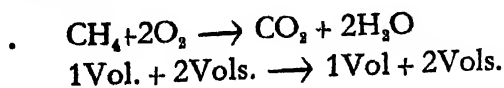
Confirm the result by determining the amount of  $\text{CO}_2$  formed. Carry out this exactly as in determining  $\text{CO}_2$  in the original sample of gas. The volume of  $\text{CO}_2$  formed by the combustion of methane equals the volume of methane present.

### Determination of oxygen :—

Close the tap E. Put a slight pressure on the gas in the burette. Turn E to connect with the pyrogallate pipette G, and pass the gas into it. Leave the gas in contact with the reagent for 5 minutes after closing E. Withdraw the gas into the burette. Sweep out the gas in the connections to the potash pipette and then pass the gas slowly into D. Take back the gas into the burette. Repeat the operation of passing the gas into D and taking back into A three or four times. Finally adjust the level of the pyro solution to mark L, close E, slightly compress the gas in A, put the burette in communication with the potash bulb by suitably turning E, measure off the volume in A after bringing the KOH solution to the marks N and O. Volume of oxygen in the sample equals the volume absorbed by the pyrogallate plus twice the volume of methane present.

NOTES :—

(1) It should be remembered that the oxygen for the combustion of methane was obtained from the gas mixture. The volume so required is twice the volume of methane present. This will be seen from the equation :—



The water formed occupies a negligible volume.

(2) A thin layer of dilute sulphuric acid. ( 1 : 10 )

is introduced into the burette and the compensator. This furnishes the necessary water which catalyses the combustion of methane and prevents the absorption of  $\text{CO}_2$  that is formed by any alkalinity of the glass parts.

(3) The mercury required in connection with gas analysis is purified from time to time by passage through a long column of dilute nitric acid of s. g. 1.1 The apparatus used is shown in Fig. 38. T is a glass-tube, 24-30 inches long and about 1 inch in diameter. It is

closed at the bottom by a one-holed cork. Through this passes a glass tube bent into the form shown and is flush with the cork. B is a beaker in which pure mercury collects, the impure mercury being made to run from the bottle I via the tubulure through the funnel into the column of dilute nitric acid in T. Above the cork there is placed a column of pure mercury about half to one inch in height. The stem of the funnel is so bent that the falling mercury takes a zigzag course in a thin stream, the stream being regulated by the pinch-clamp P. The zig-zag path

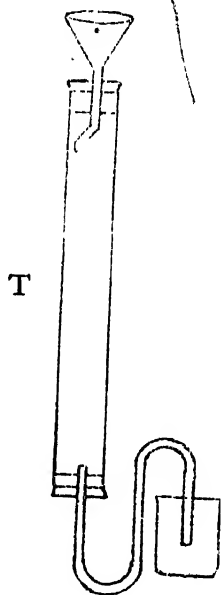


Fig. 38.

and the thin stream ensure a better purification. When poured into a porcelain dish and tilted to a side, pure mercury leaves no trail behind. Impure mercury does.

(4) The following table shows the chemical names of gases and their equivalents in mining phraseology:—

(1) Methane	Fire-damp
(2) Carbon dioxide	Chokedamp, blackdamp
(3) Carbon monoxide	White damp
(4) Hydrogen Sulphide	Stink damp

## EXPERIMENT 93 A

## Analysis of Sulphate of Ammonia.

**Moisture :—**

Weigh into a previously weighed flat bottomed dish 5 gms. of the sample and dry in an air oven to constant weight at  $110^{\circ}\text{C}$ . The loss in weight represents the moisture in 5 gms. Calculate the percentage of  $\text{H}_2\text{O}$ .

 **$\text{NH}_3$  :—****Principle :—**

When a solution of  $\text{NaOH}$  is added to  $(\text{NH}_4)_2\text{SO}_4$  solution, ammonia is liberated. This is distilled off into a measured\* volume of  $0.5\text{ N H}_2\text{SO}_4$ . The volume of acid unused is found out by titration with  $0.5\text{ N NaOH}$ . From the volume of acid used, the ammonia is calculated.

**Procedure :—**

Weigh 10 gms. of the sample into a 250 ml. beaker. Dissolve in water and transfer to a 500 ml. measuring flask. Make up to the mark. Mix well. Transfer 50 ml. of the solution by a pipette to a 500 ml. round-bottomed flask and fit up as in Fig. 15b, Experiment 39. Introduce 10 ml. of 30%  $\text{NaOH}$  solution. Dilute to 300 ml. with distilled water. Distil into 40 ml.  $0.5\text{ N H}_2\text{SO}_4$  until about 100 ml. have distilled over. Titrate with  $0.5\text{ N NaOH}$  using methyl orange as indicator.

**Example :—**

Wt. of sample 10 gms.

Solution in water made to 500 ml.

• 50 ml. solution corresponding to 1 gm. used.

Volume taken = 40.0 ml.  $0.5\text{ N-H}_2\text{SO}_4$

Volume to react }  
with excess acid } = 12.0 ml.  $0.5\text{ N-NaOH}$

Hence, 0.5 N-H<sub>2</sub>SO<sub>4</sub> used to react with NH<sub>3</sub>=28.0 ml.

1 ml. 0.5 N-H <sub>2</sub> SO <sub>4</sub>	= 0.0085 gm. NH <sub>3</sub>
28 ml. „	= 28 × 0.0085 „
% NH <sub>3</sub> in the sample	= 28 × 0.0085 × 100
	= 23.8

### Free acid :—

Dissolve 10 gms. sample in a 250 ml. beaker in 50 ml. water. Add a few drops of methyl orange. Run 0.1 N-NaOH until yellow colour appears.

1 ml. 0.1 N-NaOH=0.0049 gm. H<sub>2</sub>SO<sub>4</sub>

NOTE :—

Free acid in sulphate of ammonia is injurious both to the container bags and the soil to which it is applied as manure.

## EXPERIMENT 93 B

### Ammonia in Ammoniacal Liquor.

The ammonia in the liquor is present in solution as NH<sub>4</sub>OH, (NH<sub>4</sub>)<sub>2</sub> CO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>S. From these, NH<sub>3</sub> is evolved on boiling. It is also present in small quantities as chloride, thiocyanate, etc. From the latter the ammonia is evolved only on boiling with caustic alkalis. The ammonia in the former case is spoken as of 'free ammonia' and in the latter, as 'fixed ammonia'.

### Procedure for Free Ammonia :—

Fit up the apparatus shown in Fig. 15b (Experiment 39). Introduce 10 ml. of the ammoniacal liquor into the round-bottomed flask. Dilute to about 300 ml. with water. Distil for about 20 minutes, receiving the distillate in 20 ml. 0.5 N-H<sub>2</sub>SO<sub>4</sub>. Titrate the excess acid against 0.5 N-NaOH, using methyl orange as indicator. Calculate % of ammonia. 1 ml 0.5 N-NaOH=0.0085 gm. NH<sub>3</sub>.

### Procedure for Fixed Ammonia :—

Cool the liquid in the round-bottomed flask to Laboratory Temperature. Add 15 ml. of 30% NaOH solution to the contents of the flask and distil. Pass the distillate into 15 ml. of 0.5 N- $\text{H}_2\text{SO}_4$ . When about 100 ml. distillate have been obtained, disconnect. Titrate the excess acid as before. Calculate the % of fixed ammonia. The sum of 'free ammonia' and 'fixed ammonia' gives the 'total ammonia'.

### EXPERIMENT 94.

#### Estimation of Acidity or Alkalinity of a Lubricating oil.

The process of refinement of a mineral oil for lubrication consists in agitating it in tanks with conc.  $\text{H}_2\text{SO}_4$ , allowing to settle, drawing off the oil, agitating it with water to free it from acid and ultimately agitating it with Na-OH solution followed by water. Due to a hurrying through of the process, either  $\text{H}_2\text{SO}_4$  or NaOH may be present in the oil. The former leads to corrosion of the parts to which the oil is applied. The latter has also a corrosive action on parts of bearings which are usually made of non-ferrous alloys.

When a vegetable or animal oil is used for lubrication, the acid present is an organic acid. It is the result of decomposition of the oil due to the presence of moisture, exposure to the atmosphere, etc. Such acidity has also a corrosive action on metals.

The forms in which the acidity is expressed are :—

- (1) gms.  $\text{H}_2\text{SO}_4$  per 100 gms. oil,
- (2) gms. oleic acid „ „ (formula of oleic acid  $\text{C}_{18}\text{H}_{34}\text{O}_2$ )
- (3) number of mgs. KOH to neutralise the acid in 100 gms. of the oil.



**Principle :—**

When the oil is shaken with water in a conical flask, the acid is carried by the water which settles to the bottom as a layer. When a standard solution of KOH is added from a burette to the water layer so obtained, the acid is neutralised and phenolphthalein indicates the point at which the alkali addition is to be stopped.

**A.—Procedure for  $H_2SO_4$  in a lubricating oil :—**

Shake 100 gms. of the oil in a separatory funnel (See Fig. 41) with 100 ml. of warm water. Allow to separate. Draw off the lower acid layer into a clean flask. Repeat shaking with warm water, allow to settle, draw off the lower layer and add to the first portion. Cool to room temp. Add from a burette 0.1N-KOH using methyl orange as indicator, until a light yellow colour appears. Express the acidity in mgms. of KOH per 100 gms of the oil.

**B.—Procedure for total ( organic and inorganic ) acidity :—**

Weigh 10 gms. of the oil into a 300 ml. conical flask. Add 50 ml. of neutral 95% alcohol. Heat on the water bath to  $60^{\circ}C$ . and shake well. Add 1 ml. of a 0.5% solution of phenolphthalein and titrate with 0.1N-KOH. Express the acidity as above, i. e., in mgms. of KOH per 100 gms. oil.

**Organic acidity :—**

Subtract the value for A from the value for B. The difference represents the value for Organic acidity.

**NOTES :—**

(1) The addition of alcohol in B serves to dissolve the organic acids present. Heating to  $60^{\circ}C$  helps solution of the organic acids in that medium. Water does not dissolve the organic acids of high mol. weight.

(2) 1 ml. of 0.1N-KOH=0.0282 gm. of oleic acid.

(3) In the absence of 95 % alcohol, methylated spirit neutralised with 0.1N—KOH using phenolphthalein as indicator may be used.

### EXPERIMENT 95

#### Flash Point of a lubricating oil.

The flash point of an oil is the temperature at which the vapour issuing from the oil gives rise to a momentary flash of light when a flame is introduced into it. The test is of importance as indicating the fire risk. Oils with low flash point are obviously not suited for the lubrication of machinery in a textile mill where there is much of fibre in the form of 'fluff' floating in the atmosphere. In some cases, the flash

point gives an indication of the constitution of a blended oil. Oils from Texas and California having the same viscosity as those from Pennsylvania have a lower flash. The apparatus used is known as the Pensky-Martens tester. A sketch of the apparatus is given in Fig. 41 a. C is a silver-plated brass cup with

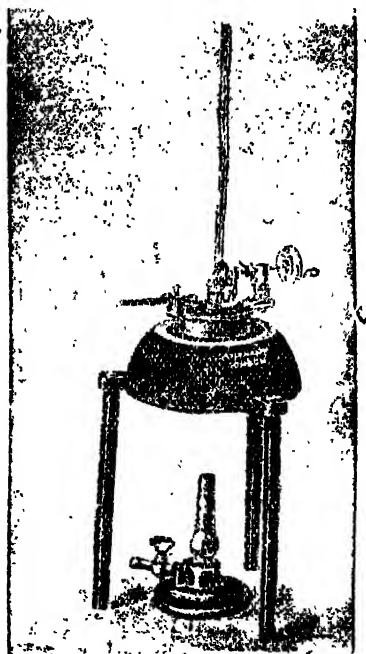


Fig. 41 a.

a flange. It has a line engraved inside all round, about 1 cm. below the top. By means of the flange

it rests on a cast iron block of metal which has a hole sufficiently large for the reception of the cup and to have an air space all round the cup. The block of metal is supported on a tripod. A Bunsen burner heats the block and thus the air surrounding the cup forms an air bath. A cover with three slots fits on to the cup. Through the centre of this passes a shaft which has two sets of blades fitted to it. One set, the lower one, stirs the oil when a determination is being made and the other stirs the air-vapour mixture. At the top of the shaft is a bevelled gear wheel engaging with a second bevelled gear wheel fixed at the end of a horizontal shaft. By means of the handle H, the stirrer shaft S can be so rotated that the stirrer moves or remains stationary. When the gears do not engage each other, a brass cover with slots similar to those on the lid proper can be so moved that the test flame from the burner is made to dip momentarily into the vapour. Normally the slots on the topmost lid do not come opposite the slots on the cover proper, so that during an experiment, the vapour is confined in the cup. As indicated in the notes below, the cup, the spindle with the two sets of vanes and the cover must be wiped, after each experiment, with pieces of filter paper, until clean.

There are two holes in the cover with slit, cylindrical projections. These are for the insertion of thermometers. The bulb of one is immersed in the oil and that of the other is in the vapour space.

#### **Procedure:—**

Fill the cup with oil up to the gauge mark. About 75 ml. of the oil will be required.

Place the cover with the thermometer in position.

Light the injector burner. The gas should be so adjusted that the flame is about  $\frac{1}{8}$ " long. Heat the apparatus by a Bunsen burner. Stir so that the stirrer makes one revolution per second. The rise of temperature should be 7°–8° F. per minute. When the temperature of the oil is approaching that at which the oil flashes, the ignition burner is injected for about 2 seconds every half minute until a distinct flash is seen within the cup. The flash is quite distinct if the test be performed in a darkened room. The vapour from some oils extinguishes the injector flame at the beginning but as the temperature of the oil rises, and approaches the flash point, there will be no difficulty experienced.

NOTES :—

(1) The tester should not be moved from place to place after it is filled with oil. The sides are wetted above the gauge mark by the splashing of the oil, if this precaution is not observed.

(2) For all oils above 120°F. flash point, this is the tester most widely used. For oils having a low flash point, the Abel apparatus is used. See Expt. 96.

(3) Empty out the oil. Wipe out with pieces of filter paper the oil that is still adhering to the wall of the cup. Rinse the same with a few ml. of petroleum ether or ethyl ether. Blow into it with footbellows a blast of air. This will leave the cup clean and free from vapour of the rinsing liquids. The silverplating is removed by rough cleaning with sand.

## EXPERIMENT 96.

**Determination of Flash Point of an oil using the Abel apparatus.**

This apparatus is shown in Fig. 41 b. This has been designed for determining the flash-point of oils having a flash-point ranging from  $60^{\circ}$  F to  $150^{\circ}$  F. It consists of a cylindrical copper screen mounted on feet

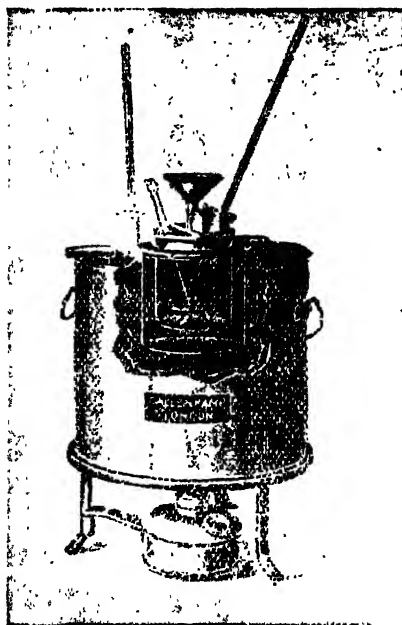


Fig. 41 b.

which serve to support the copper water vessel. This has a central cavity for the reception of the oil cup. This is of smaller dimensions than the cavity so that the cup, during an experiment, is heated by an air bath. This cup has a tight fitting cover which sockets on to it. A thermometer having a range of  $60^{\circ}$ F. to  $150^{\circ}$ F. is secured in a fixed brass collar. This in turn fits into a socket

in the cover. If the collar is pushed home against the socket, the bulb of the thermometer always occupies a definite position in the oil cup, thus making it possible to obtain nearly concordant results on the same oil. A clock-work mechanism is provided which makes it possible to introduce the test flame in the vapour space at regular intervals of temp. through slots on a sliding cover, which slots come opposite similar slots made on one half portion of the cover proper. Normally the slots in the latter remain covered by the unslotted portion of the sliding cover. A small bead of 0.15 inch diameter is provided on the cover of the cup. This is to indicate the size of the test flame to be used. This may be either an oil flame or a gas flame. A screw clip is provided on the rubber connection to the gas-tap to enable one to regulate the gas supply and thus obtain the flame of the required size. The cup has a gauge pin. It is filled with oil to the tip of the pin when making an experiment.

The water jacket is provided with a thermometer on which the 130 degrees Fahr. mark is clearly defined. This water bath is heated by a lamp mounted on a swivel attached to one of the legs of the stand. When a number of determinations have to be made, the water-bath may be lifted out of its support and heated by a low Bunsen flame to 130°F.

#### **Procedure :—**

Place the apparatus in a position free from draughts. Pour water into the funnel until the water overflows through the spout of the bath. Heat the water to 130°F and place the bath in the cylindrical support. Cool the oil to 60°F., in case it is at a higher temperature. ( Iced water or water stored in a fresh mud pot may be used for the purpose. ) Pour oil into the cup until the tip of the gauge pin is just covered. Insert the

thermometer into the socket in the cover. Put this on the cover with the slide closed. Place the cover in position so that it tightly closes the cup. Apply the test flame for every degree rise in temp. The flash point is the lowest temperature at which a momentary blue flame is seen to spread over the whole surface of the oil. This is usually accompanied by a slight report, a 'pop' and the test flame is extinguished.

NOTES :—

(1) The same precautions in cleaning the cup, the cover and the thermometers as with the Pensky-Martin apparatus are to be taken before introducing a fresh sample of oil for examination.

(2) When oils with a flash point above 150°F. are to be tested, it is permissible to introduce in the air chamber in the water-bath cold water to a depth of 1.5 inches, the water in the jacket itself being at 120°F. Insert the cup filled with oil to the gauge pin and proceed as before. Introduce the test flame, in the initial stages every 3 degrees rise, but at one degree intervals after for some minutes when the rise in the thermometer slows down.

(3) A fresh portion of the sample must be used for each test.

## EXPERIMENT 97.

### To find the Viscosity of an Oil by the Redwood Viscometer.

The time of flow of 50 ml. of oil at 70°F. expressed in seconds is the viscosity of the oil when measured by this instrument. The object of the test is to find whether the oil applied for lubrication is sufficiently viscous to adhere to the bearing to which it is applied and to lessen the friction between the moving parts or it is so

thin as to be squeezed out from between the moving parts on account of the pressure on the bearing.

The instrument is shown in Fig. 42.

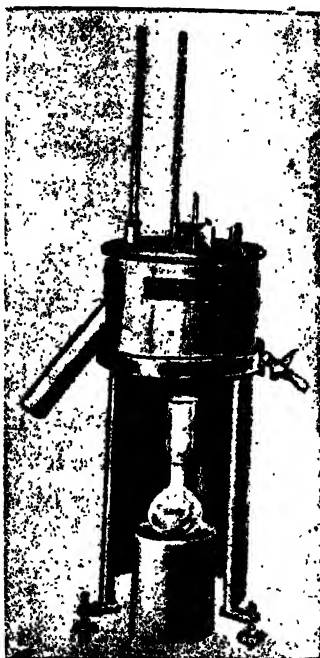


Fig. 42.

It consists of a silvered copper cylinder about 1 inch in diameter by about  $3\frac{1}{2}$  inch in depth furnished with an agate jet. The cylinder is the oil container. The exterior of the agate jet and its metal seating are made slightly conical and the jet having been once fixed in position, no dislodgment nor leakage can occur, even when the apparatus is used at high temperatures. The copper bath which surrounds the oil cylinder and into which the oil cup screws is of such a depth that the level of the bath liquid can be made to coincide with the level of oil without any danger of overflow or splashing into the oil cylinder. A



copper tube, closed at one end, projecting at an angle of  $45^\circ$  from the side of the bath, near the bottom, provides a means of

heating the bath liquid, and, by the use of a revolving agitator, the heated liquid rising from the copper tube can be uniformly distributed through the bath. The agitator which carries a thermometer or indicate the the temperature of the bath is so constructed that splashing is prevented. The oil cylinder is provided with a small silvered brass sphere attached to a wire by means of which the agate hole is closed or opened. A short standard attached to the oil cylinder carries a clip to support a thermometer in the oil. Inside the oil cylinder and at a short distance from the top is a small bracket terminating in an upturned point. The instrument is supported on a tripod stand with levelling screws. A circular spirit level is provided to fit on the top of the oil cylinder.

#### **Procedure :—**

About 135 ml. of the oil will be required. Pour the oil into the cylinder so that it comes up to the gauge point.

The oil in the cylinder is stirred by moving the thermometer backwards and forwards in the oil so as not to splash the oil. The outer liquid also should be kept well stirred. Fix the thermometer about halfway between the centre and the wall of the cylinder. Lift the ball off. Start the stop-watch. Note the time of efflux of 50 ml. in seconds. Surround the 50 ml. flask with a liquid at the same temperature as the oil in the cylinder or lag it with cotton-wool. This ensures that the 50 ml. collected is at the same temperature as the oil in the cup.

The following table shows the temperature of the liquid in the bath and the temperature at which the viscosity measurement is to be made :—

Temperature of liquid in the bath.	Temperature at which viscosity is required.
59.5°F.	66°F.
60.5°F.	60°F.
142°F.	140°F.
205°F.	200°F.
260°F.	250°F.
Class of Oils.	Temp. at which viscosity measurement is made.
Engine oils	60°, 70° and 140° F.
Cylinder oils	200°F and 250° F.
Thick Axle oils	80°F.

NOTES :—

( 1 ) The viscosity measurement at different temperatures serves to detect the presence of an adulterant such as soap. The fall of viscosity with rise of temp. is far greater in the case of a 'soap thickened' oil than with an oil not so thickened.

( 2 ) A solution of aluminium soap in a mineral oil is used as an adulterant. Oils so adulterated are referred to as 'soap-thickened' oils.

( 3 ) To expedite a determination, the oil may be heated up to the required temp. and then poured into the cup.

( 4 ) The 50 ml. mark is placed high above the neck, facilitating disengagement of air bubbles.

## EXPERIMENT 98.

**Percent of Vegetable or Animal oil in a Lubricating oil :—****Object :—**

A pure mineral oil does not adhere to the surface of a steam engine cylinder run on saturated steam. A small addition of 2 to 3% of vegetable oil to a mineral oil produces the necessary adhesion. But more than this is harmful, leading to the corrosion of the cylinder walls due to the liberation of large quantities of fatty acids from the animal or vegetable oils by the action of steam. The test serves to detect any adulteration.

**Principle :—**

The determination is based on the fact that vegetable and animal oils are saponified by treatment with a measured excess of a standard alcoholic solution of caustic soda or potash, the mineral oils remaining unaffected by such treatment. The term 'saponification' is applied to a chemical change leading to the production of soap, which is the sodium or potassium salt of an organic acid and glycerol.

The excess alkali is subsequently titrated with 0.1N HCl. The volume of this deducted from the volume of 0.1N-KOH originally used for saponification provides the basis for the calculation of the vegetable or animal oil present in the lubricating oil supplied.

**Definition.** By the term the 'saponification value' of an oil is meant the number of milligrams. KOH required to saponify 1gm. of the oil.

**Solutions required :—**

- (1) Dissolve 2.8 gms. of KOH in 100 ml. of

rectified spirit of s.g. not over 0.81. This solution will be about 0.5N strong.

(2) 0.5 N-HCl.

**Procedure:-**

Weigh 1.5 gms. of the sample of oil into a 200 ml. flask shown in Fig. 44. Add 25 ml of 0.5N alcoholic potash. A tube 3 ft. long and  $\frac{1}{4}$  inch bore serves as a condenser for the alcohol. Place the flask in a boiling water bath for  $\frac{1}{2}$  to 1 hour at the end of which time the saponification is complete. At the same time treat a second flask similarly but without

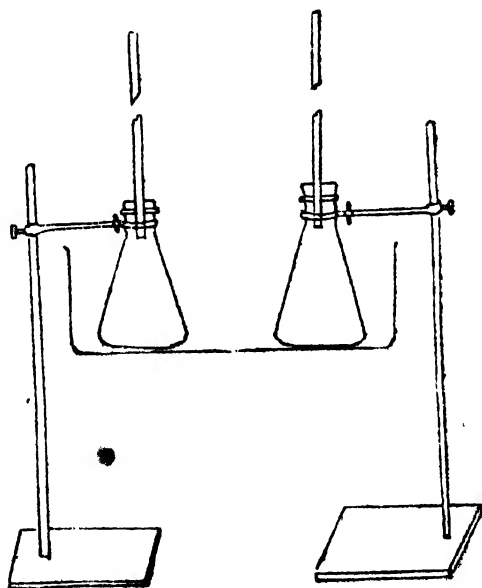


Fig. 44.

the oil. This serves as a control test. During the heating of the sample, the potash may absorb  $\text{CO}_2$  from the air or some of it may react with the glass vessel in which the saponification is made. The two flasks are

cooled, a few drops of phenolphthalein are introduced into each and they are then separately titrated with 0.5 N. HCl.

Wt. of flask = 46.4534 gms.  
 „ „ „ with oil = 48.4539 „  
 Hence weight of oil taken = 2.0005 „  
 25 ml. of KOH (Control) requires 22.9 ml. of 0.5 N-HCl  
 25 ml. of KOH (Sample) requires 21.3 ml. „ „  
 1 ml. of 0.5 N HCl = 0.28 gm. KOH  
 1.6 ml. „ = 28 × 1.6 mgms. KOH  
 2.0005 gm. oil saponified by 44.8  
 $\therefore 100 \text{ gms. „ } \frac{44.8 \times 100}{2.0005} = \frac{44.8 \times 100}{1000 \times 2.0005} \text{ gm}$   
 $\% \text{ Saponification value of the lubricant } \left. \vphantom{\frac{44.8}{10 \times 2.0005}} \right\} = \frac{44.8}{10 \times 2.0005}$   
 $= 2.24$

Saponification value of the lubricant is 22.4. See the definition.

Saponification value of the fatty oil known to be present in the oil is 180.

If 180 is the saponification value, fatty oil present is 1 gm.

22.4                    "                    "                    "                    "                     $\frac{22.4}{180}$  "

1 gm. lubricant contains  $\frac{22.4}{180}$  gm. fatty oil

$$\therefore 100 \text{ gms } ,, \quad ,, \quad \frac{22.4}{180} \times 100 = \frac{112}{9} = 12.4 \text{ gms.}$$

**% Fatty oil in the sample is 12.4.**

**Procedure when the nature of the fatty oil present is not known :—**

Transfer the product of saponification to a wet separating funnel (Fig. 43.) using about 30 ml. water

and 30 ml. of petroleum ether ( boiling-point below  $80^{\circ}\text{C}$  ) to rinse the flask. The mixture is shaken, allowed to separate and the lower layer drawn into a second tap funnel.

Shake the separated soap solution with further charges of petroleum ether until it is freed from oil. Evaporate the soap solution to dryness in a porcelain dish on a steam bath, redissolve in water, acidify with a slight excess of 1.15 s. g.  $\text{H}_2\text{SO}_4$  and heat until the fatty acids separate.

Transfer the fatty acids and sulphuric acid and sulphate to a tap funnel. Cool. Shake with methylated ether. This dissolves the fatty acids, and, being lighter, floats on the top of the aqueous layer. Draw this off. Shake with more water and draw off the lower water layer. Repeat treatment with water until the ethereal



Fig 43.

layer is free from mineral acid. It will be free from the mineral acid when a few ml. of the aqueous layer do not yield a precipitate with a solution of  $\text{BaCl}_2$ . Transfer the ethereal layer to a weighed flask. Distil off the ether on the steam bath. Heat on the steam bath until the flask and the acid are constant in weight. Multiply the % of fatty oil by 1.05 to get the % of fatty oil present in the lubricating oil.

Wash the petroleum ether solution of the mineral oil in the first tap funnel with small charges of water until free from soap. These washings are to be added to the main soap solution before taking to dryness.

If any obstinate emulsion forms and the soap and the mineral oil solutions do not separate sharply, add a few drops of alcohol. This will effect a sharp separation into layers.

Transfer the petroleum ether solutions to a weighed flask, distil off the petroleum ether on a steam bath, heat to constant weight. This gives the weight of unsaponifiable mineral oil.

In cases where a precipitate of asphaltic matter is noticed either in the soap, or the ether solution, it is filtered out, washed, weighed and added to the weight of unsaponifiable oil.

**NOTES :—**

(1) When the unsaponifiable oil preponderates as shown by the test, the direct estimation of fatty acids must be made in estimating the proportion of saponifiable matter. When the saponifiable matter preponderates, the direct estimation of unsaponifiable oil is to be made.

(2) When a small percentage of saponifiable matter is found, it should be remembered that this may be due to natural petroleum acids and not to added fatty matter.

**EXPERIMENT 99.**

**Determination of the "Iodine Number" of Castor Oil.**

( Hubl's Method )

**Definition**—The iodine number or value of an oil is the number of grams of iodine absorbed by the unsaturated compounds present in 100 grams of the oil.

**General remarks**—Castor oil is a Government Store Material. Like all materials, purchased by the Government, the purchase of this material also is based on chemical examination. The iodine number of the oil is 84.. It is an ideal lubricant for aero-engines.

**Principle**—When a weighed quantity of the oil dissolved in pure chloroform is treated with a measured excess of iodine chloride solution obtained by mixing a solution of iodine in alcohol with a solution of mercuric chloride in alcohol, the unsaturated fatty acids of the oil absorb the iodine. The amount absorbed is obtained by titrating the excess of iodine against standard sodium thiosulphate solution.

**Reagents :—**

(1) Iodine solution : Dissolve 10 gms. of iodine in 200 ml. of 95% alcohol. Mix this solution with an equal volume of mercuric chloride prepared by dissolving 12 gms. of the salt in 200 ml. of alcohol of the same strength. Keep the mixture in a glass stoppered bottle (amber colour). Use the mixed solution for an estimation after standing it for at least 12 hours in the dark.

(2) 0.1N  $K_2Cr_2O_7$ .

(3)  $Na_2S_2O_3$  solution. This is standardised against the dichromate solution.

(4) An approximately 15% solution of pure potassium iodide in cold recently boiled distilled water.

(5) Freshly prepared starch solution : 0.2 gm. in 50 ml. of water.

(6) Pure chloroform.

(7) Cold recently boiled distilled water.

**Procedure :—**

Pour a small quantity of castor oil into a clean dry specific gravity bottle. Weigh. Transfer a portion to a clean, dry 250 ml. glass stoppered bottle. Weigh the S. G. bottle again. Difference=oil taken. Add 20 ml. of chloroform. Shake. When the oil has dissolved, introduce 10 ml. of the mixed iodine mercuric chloride



solution. Shake the mixture gently. Allow to stand, in a cool, dark place for 3--4 hours. Into a second glass stoppered bottle previously cleaned and dried, introduce 20 ml. of chloroform and 10 ml. of the iodine mercuric chloride mixture and allow to stand by the sample run in the cool, dark room for the same length of time. This test serves as the blank run. At the end of this time, remove from the dark room. To each of them add 100 ml. of cold water ( reagent above ) and then 20 ml of potassium iodide solution ( 4 ). In case a red precipitate of mercuric iodide appears, add more of the KI solution until it disappears. Run the thiosulphate from a burette rapidly until the liquid is pale yellow ; then introduce 2 ml. of the starch solution and finish the titration. The thiosulphate solution must be run in until the blue colour is just discharged. The difference between the volumes of the thiosulphate solution required for the sample and the blank gives the amount of iodine absorbed. From this the % is calculated. To find the value of 1 ml. of  $\text{Na}_2\text{S}_2\text{O}_3$  solution in terms of iodine, proceed as follows:— Run from a burette 25 ml. of 0.1N- $\text{K}_2\text{Cr}_2\text{O}_7$  solution into a 250 ml. conical beaker. Add 20 ml. of KI solution and 5-10 ml. of 1.1 s.g. HCl. Add the thiosulphate from a burette until the deep red colour of the liberated iodine changes to light yellow. Introduce 2 ml. of starch and continue the addition of the thiosulphate until the blue colour is just discharged. Normality of the thio solution is  $\frac{25 \times 0.1}{n}$ , n being the number of ml. of the thio sulphate solution. 1 ml. of 0.1N thiosulphate=0.0127 gm. Iodine.

## CHAPTER XI.

### Sampling.

#### General:—

Engineering materials are manufactured to conform to certain specifications laid down by organisations representative of manufacturers, users and scientists. These specifications cover both chemical composition and physical and mechanical properties. The former is determined by the analysis of a few grams of the material representing tons of it. Unless the few grams of sample are thoroughly representative of the lot, great hardship will result to the manufacturer on account of rejection of the lot, when the chemical analysis, performed on a sample chosen at random, reveals that the material does not conform to the accepted specification. Or, it may be that the chemical composition shows the material to be good but that in service it fails involving loss of lives as when a boiler shell bursts or the rail of a track breaks.

#### Sampling of Steel :—

To guard against misleading results being arrived at, procedures have been developed for the sampling of steel while yet in the molten condition. They consist in collecting a sample in a spoon as the metal is being run out from the ladle into the moulds. If, for example, the capacity of a ladle is 60 tons, samples are drawn one for each 20 tons of metal poured into the moulds. If the moulds are each of capacity 5 tons, then samples are taken out as the metal is being run into the fourth, eighth and twelfth moulds. The moulds used for sam-

pling are cast either from iron or steel. Fig. 45 shows one such mould. When the metal has solidified, the mould is tipped. The test piece is allowed to cool in air, the number of the heat and the furnace number are stamped on it. A  $\frac{3}{4}$ " diameter drill is used for drilling a hole from the bottom of the piece. The drillings from the first half inch depth hole are rejected. Only drillings from below the first half-inch hole are used for analysis. The drillings from each of the three test-pieces relating to one particular heat are kept in separate bottles. They are each separately analysed.

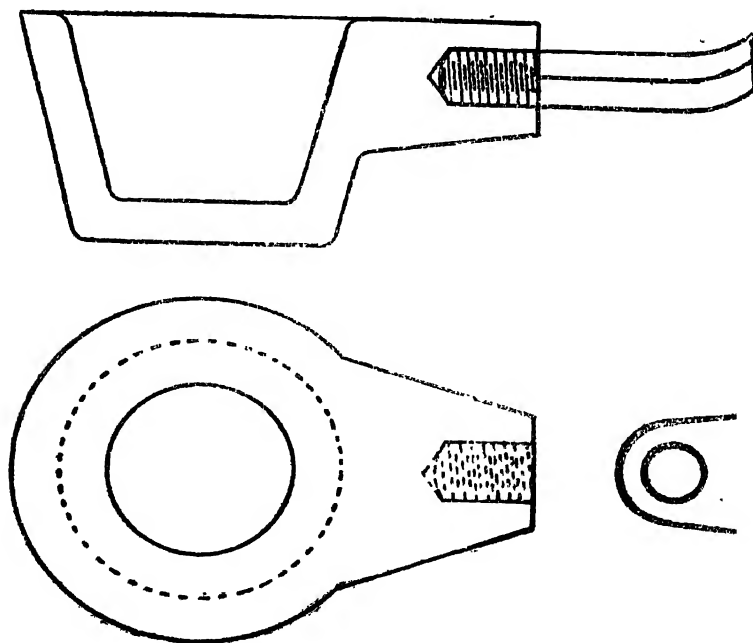


Fig. 45.

In the case of steels containing tungsten and chromium, an annealing treatment is necessary before the test-pieces can be drilled. This consists in heating them in a furnace to 700 to 800°C. and cooling them slowly in the furnace.

Hadfield steels containing high percentages of manganese can be drilled with a high speed drill when they are at a dull red heat.

For carbon determination, drillings passing through a 20 mesh sieve and retained on a 40 or 80 mesh sieve are used. Those retained on the 20 mesh sieve are used for the determination of S, P, Mn and Si.

**Sampling of Blister or Refined Copper :—**A templet covering the entire surface of the ingot is used. Drillings from the first  $\frac{1}{4}$ " hole are rejected. Those obtained from the deeper holes on the top surface of the ingot are mixed with those obtained from the bottom surface of the ingot, using the templet, the holes made being in all cases, of the same depth. This procedure is particularly necessary in the case of the metal containing silver and or gold.

### **Sampling of Gold and Silver bullion :—**

The piece is sawn through right in the middle, the sawings melted in a graphite crucible, and a sample is taken out by means of a scooped—out charcoal rod or spoon. This is granulated by pouring into a bucket of water. The grains are used for assay. This process is known as taking a 'dip' sample.

**Sampling of Iron from the Blast Furnace:—**The procedure consists in taking out a sample as the metal is running out from the furnace. Two samples are generally taken, by means of a spoon, as one-third and two thirds of the metal have run out. The metal is poured into a cast-iron mould. This is tipped when the metal has solidified. The two pieces for each tap are separately drilled and equal weights of drillings from each piece are mixed and analysed. In the case of samples low in silicon and high in combined carbon, the test-

pieces which are about 3" long and about  $\frac{1}{4}$ " square in section are crushed to powder in a specially hardened steel mortar by means of a sledge hammer, 30-40 lbs. in weight. It is sieved to pass through an 80 mesh sieve. The + 80 portion is crushed until it completely passes through the sieve ; the portions are well mixed and then analysed. Fracture of the cast piece indicates whether it is to be drilled or powdered.

### **Sampling of Ores, Coal, etc.**

**General :—**The methods evolved for the sampling of ores, have for their object equity and fairness to those owning deposits, working them and submitting them to smelting companies for winning the metals. Unlike the practice in this country where the same company mines its ore and works it up into finished metallic manufactures for sale to the consumers, the practice in the U. S. A., England, Germany, etc., countries has been for one company to work ore deposits and tender the ore to a second company which is working up the ore into metal. The conditions are similar to those that obtain in our country in regard to the sale of sugar-cane to sugar refineries. The price paid to the cane-grower is on the basis of the sugar content of the juice obtained from his cane. While it is somewhat a simple matter to draw a sample of juice and examine it for its sugar-content, the case is different in the case of ores. The deposits, say, of copper ore, lead ore, etc., vary greatly in regard to their contents both of the basic metals for which they are worked and the precious metals which they contain. Hence elaborate procedures have been evolved and prescribed for the sampling of the above ores.

They are also necessary for maintaining control on

the efficiency of the processes of recovery and for drawing up a balance sheet of the input of materials into furnaces and the output of metals therefrom.

**Sampling of Iron ore** :—As the ore is being unloaded from wagons, one basket is set apart for every 19 baskets. For a 20 ton wagon, the sample thus collected will weigh about a ton. This is thoroughly mixed by forming a conical pile with the help of a shovel. The ore is so piled that one shovelful after another is allowed to slide from the shovel always at the apex of the cone. This is then formed into a rectangular pile about 9' long 6' broad and 5' deep. In forming this pile from the conical pile, a certain regularity is observed both in the dismantling of the pile and the forming of the rectangular pile. The object is to ensure thorough mixing. For example, a shovelful is spread, then another in continuation of the first and so on until the desired length of 9' is completed. Then the shovelfuls are spread in the reverse direction to the original until the 5' deep column is reached. This rectangular pile is cut into four equal quarters. Any two diagonally opposite quarters are mixed, coned and quartered. In crushing down large size lumps to small size lumps, the point that is borne in mind is that at each successive stage of crushing, the weight of material taken shall be a definite fraction of the weight of the original quantity. The crusher used is the Blake jaw crusher. See Fig 46.

If the original size of the pieces is, say, a 2" cube, each and if the size of the pieces of crushed material is 1" cube each (i.e.,) the size becomes halved, then the weight of crushed material to be taken and further reduced in size is  $(\frac{1}{2})^3$  i.e.,  $\frac{1}{8}$  of the original quantity. When this condition is satisfied, each original lump, rich or poor, has contributed its quota to the sample. As it is

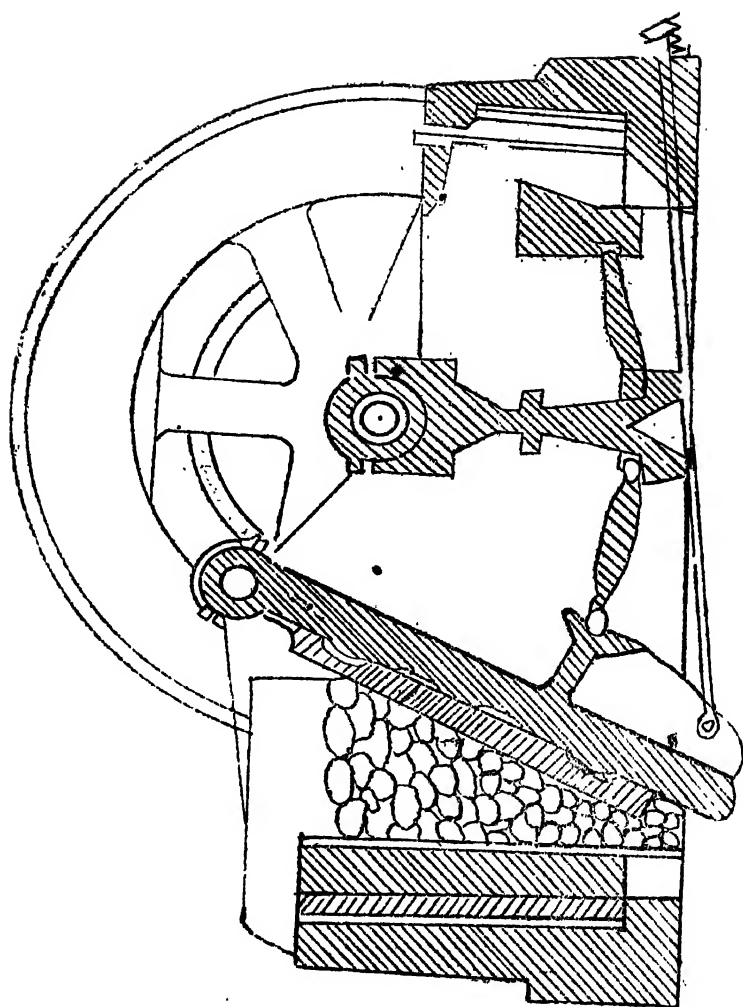


Fig. 46

not possible to be counting the number of particles or lumps at each stage of crushing, the only way of ensuring that each lump has contributed to the sample is to take  $1/n^3$  of the original quantity of the ore if the diameter of the reduced particle is  $1/n$  of the diameter of

the original particle. When the sample is reduced to about  $\frac{1}{2}$  lb. by the above process of crushing, coning and quartering, the entire quantity is powdered on a bucking board with a muller, Fig. 47, and passed through a 100 mesh sieve. This is stocked in a corked or stoppered container and analysed. The bucking board and muller are of hardened chrome steel. The weatherhead pulverizer may be substituted. See Figs. 48 a and b.

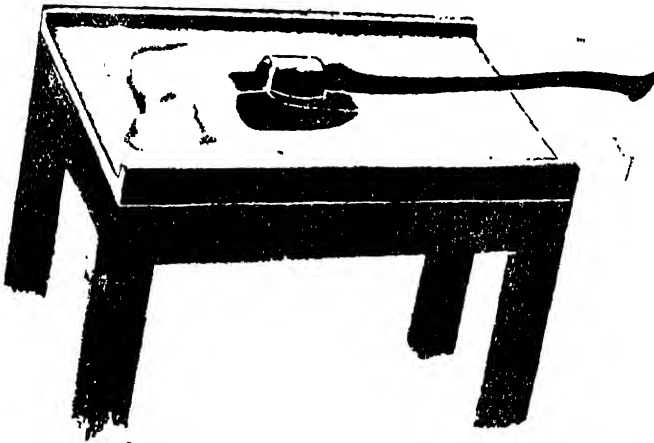


Fig. 47.

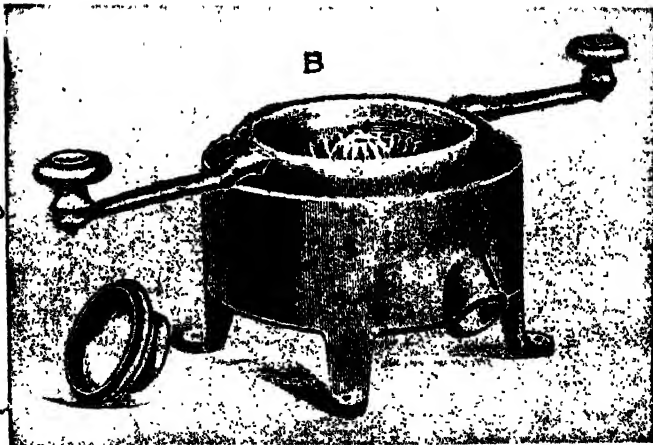


Fig. 48 a.



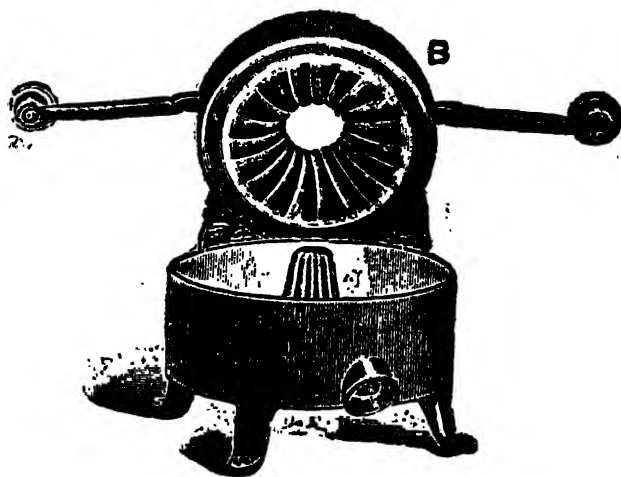


Fig. 48 b.

To expedite the process of quartering ( i.e., ) dividing the rectangular pile into four quarters and taking the diagonally opposite quarters for further reduction, a sampler known as the Jones Riffle Sampler shown in Figs. 49 a and b is employed. This is made in several sizes, the openings in each one being uniform.

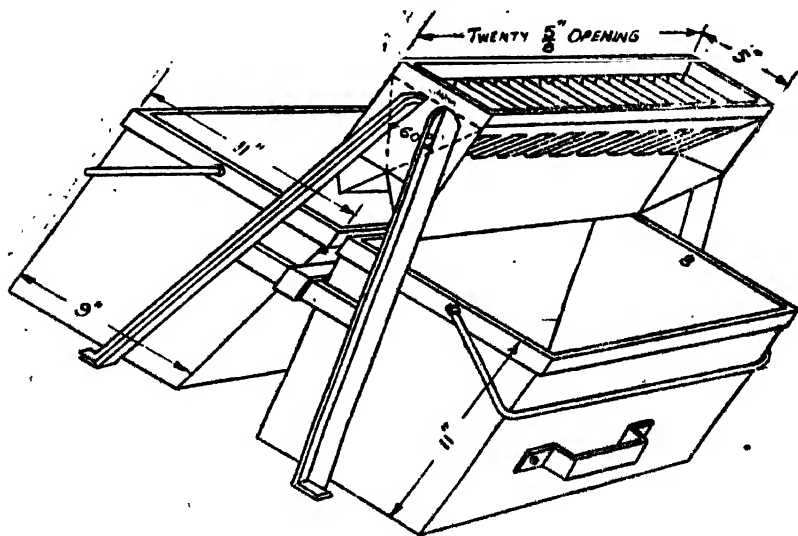


Fig. 49

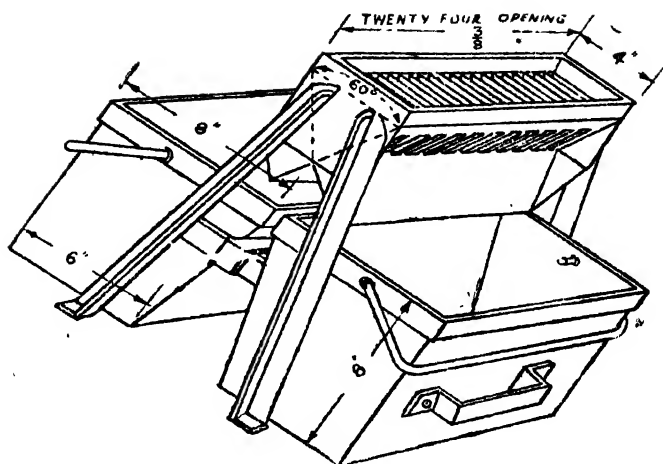


Fig. 49b.

### Sampling of Coal:—

As in the case of iron ore, samples are drawn at the time of unloading of coal from wagons, one basket of coal being set apart for every 19 baskets of it sent to the boiler plant or other unit of a works. The sample is formed into a conical pile, always dropping shovelfuls at the same apex point to ensure uniformity of mixing. It is then pressed down at the apex, then formed into a rectangular pile, divided into four quarters, any two of the diagonally opposite quarters being taken for a sample. This is further crushed, coned and quartered until a quantity weighing about 30 lbs. is obtained. The American Society for Testing Materials gives the following schedule re reduction in size :—

Weight of sample  
to be divided, lbs.

Largest size of coal and im-  
purities as estimated by the eye,  
allowable in sample before di-  
vision ( inches ).

1000 or over	1
500.....	3/4
250.....	1/2
125.....	3/8
60.....	1/4
30.....	3/16 or to pass a 4760-micron ( No. 4 ) sieve.

The 30 lb. sample is passed through a Jones riffle sample with  $\frac{1}{2}$  or  $\frac{5}{8}$ " divisions. The 15 lb. quantity is powdered in the weatherhead pulverizer and passed through a riffle with  $\frac{1}{4}$  to  $\frac{3}{8}$ " divisions for reducing the quantity passing through the 250 micron (No. 60) sieve to the laboratory sample which is about 50 gms. This is immediately transferred to a glass-stoppered bottle.

Sampling at the working face of a seam as laid down by the Indian Coal Grading Board preparatory to analysis :—

The face of the coal seam to be sampled is first dressed down from top to bottom and fresh surface exposed. Two vertical lines about a foot apart are chalked out from top to the bottom of the section of the seam to be sampled. The stone and shale bands which are usually picked out from the loading are chalked out between the vertical lines. Coal about 6 to 8 inches in depth is then cut from the top to the bottom of the section and bands of shale or stone, etc., are left in tact in the seam. The coal is crushed, coned and quartered until the sample weighs about 30 lbs.

This is then put in an air-light container, sealed and sent to the Government Test House at Alipore, Calcutta, where it is further reduced to the laboratory sample of 50 gms. passing through a 60 mesh sieve for analysis.

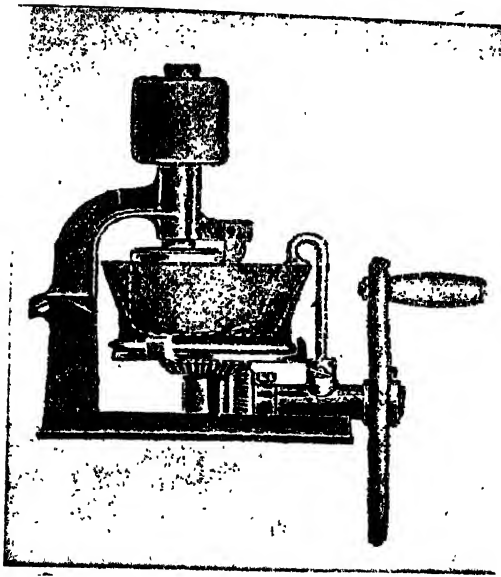


Fig. 50.

Manganese ore is sampled much in the same manner as iron ore.

A laboratory type edge-runner is shown in Fig. 50.

## **Books for Further Study**

1. 'The Chemical Analysis of Steel Works' Materials'.  
by F. Ibbotson.
2. 'The Analysis of Non-Ferrous Metals and Alloys' by  
F. Ibbotson and L. Aitchison.
3. 'The Metallurgist's Manual' by T. G. Bamford and  
H. Harris.
4. 'Metallurgical Analysis' by N. W. Lord and D.  
Demorest.
5. 'The Sampling and Chemical Analysis of Iron and  
Steel' by O. Bauer and E. Deiss translated  
by W. T. Hall and R. S. Williams.
6. 'Assaying in Theory and Practice' by E. A. Wraight.
7. 'Notes on Assaying' by R. W. Lodge.
8. 'A Text Book of Fire Assaying' by E. E. Bugbee.
9. 'Text Book of Rand Assay Practice' by F. Moir  
and G. H. Stanley.
10. 'Quantitative Chemical Analysis by Electrolysis' by  
A. Classen and W. T. Hall.
11. 'Tested Methods of Mineral Analysis' by B. T. Kitto.
12. 'Manual of the Chemical Analysis of Rocks' by H.  
S. Washington.
13. 'Analysis of Coal and Its By Products' by S. R.  
Illingworth.
14. 'Methods of Air Analysis' by J. S. Haldane.
15. 'Gas Analysis' by L. M. Dennis.
16. 'Standard Methods of Testing Petroleum And Its  
Products' by the Institute of Petroleum Technolo-  
gists, London.

**TABLE 1-**  
**International Atomic Weights.**  
**1933.**

	Atomic Number	Atomic Weight		Symbol	Atomic Number	Atomic Weight.
1. Aluminium	13	26.97	44. Molybdenum	Mo	42	96.0
2. Antimony	51	121.76	45. Neodymium	Nd	60	144.27
3. Argon	A 18	39.944	46. Neon	Ne	10	20.183
4. Arsenic	A 33	74.93	47. Nickel	Ni	28	58.69
5. Barium	B 56	137.36	48. Nitrogen	N	7	14.003
6. Beryllium	B 4	9.02	49. Osmium	Os	76	190.8
7. Bismuth	B 83	209.00	50. Oxygen	O	8	16.00
8. Boron	B 5	10.82	51. Palladium	Pd	46	106.7
9. Bromine	B 35	79.916	52. Phosphorus	P	15	31.02
10. Cadmium	Cd 48	112.41	53. Platinum	Pt	78	195.23
11. Calcium	Ca 20	40.08	54. Potassium	K	19	39.10
12. Carbon	C 6	12.00	55. Praseodymium	Pr	59	140.92
13. Cerium	Ce 58	140.13	56. Radium	Ra	88	225.97
14. Cesium	Cs 55	132.81	57. Radon	Rn	86	222.
15. Chlorine	Cl 17	35.457	58. Rhenium	Re	75	186.31
16. Chromium	Cr 24	52.01	59. Rhodium	Rh	45	102.91
17. Cobalt	Co 27	58.94	60. Rubidium	Rb	37	85.44
18. Columbium	Cb 41	93.3	61. Ruthenium	Ru	44	101.7
19. Copper	Cu 29	63.57	62. Samarium	Sm	62	150.43
20. Dysprosium	Dy 66	162.46	63. Scandium	Sc	21	45.10
21. Erbium	Er 68	167.64	64. Selenium	Se	34	79.2
22. Europium	Eu 63	152.0	65. Silicon	Si	14	28.06
23. Fluorine	F 9	19.00	66. Silver	Ag	47	107.880
24. Gadolinium	Gd 64	157.3	67. Sodium	Na	11	22.997
25. Gallium	Ga 31	69.72	68. Strontium	Sr	38	87.63
26. Germanium	Ge 32	72.60	69. Sulphur	S	16	32.06
27. Gold	Au 79	197.2	70. Tantalum	Ta	73	181.4
28. Hafnium	Hf 72	178.6	71. Tellurium	Te	52	127.5
29. Helium	He 2	4.002	72. Terbium	Tb	65	159.2
30. Holmium	Ho 67	168.5	73. Thallium	Tl	81	204.39
31. Hydrogen	H 1	1.0078	74. Thorium	Th	90	232.72
32. Indium	In 49	114.8	75. Thulium	Tm	69	169.4
33. Iodine	I 53	126.92	76. Tin	Sn	50	118.70
34. Iridium	Ir 77	193.1	77. Titanium	Ti	22	47.90
35. Iron	Fe 26	55.84	78. Tungsten	W	74	184.0
36. Krypton	Kr 36	83.7	79. Uranium	U	92	238.14
37. Lanthanum	La 57	138.92	80. Vanadium	V	23	50.95
38. Lead	Pb 82	207.22	81. Xenon	Xe	54	131.3
39. Lithium	Li 3	6.940	82. Ytterbium	Yb	70	173.5
40. Lutecium	Lu 71	175.0	83. Yttrium	Y	39	88.92
41. Magnesium	Mg 12	24.32	84. Zinc	Zn	30	65.38
42. Manganese	Mn 25	54.93	85. Zirconium	Zr	40	91.22
43. Mercury	Hg 80	200.61				

TABLE 1 A.

Specific Gravity of Aqueous Hydrochloric Acid Solutions.  
Water at 4°C. is taken as unity.

S. G. measurements refer to acids at 20°C.

S. G.	Percent HCl	Approximate Normality
1.018	4	1.11
1.047	10	2.87
1.094	20	6.02
1.129	26	8.04
1.198	40	13.13

TABLE 1 B

S. G. of Aqueous Nitric Acid Solutions at 20°/4° C.

S. G.	Percent HNO <sub>3</sub>	Approximate Normality	S. G.	Percent HNO <sub>3</sub>	Approximate Normality,
1.025	5	0.81	1.200	33	6.28
1.054	10	1.27	1.400	67	14.89
1.115	20	3.54			

TABLE 1 C.

S. G. of Aqueous Sulphuric Acid Solution at 20°/4° C.		
S. G.	Per Cent H <sub>2</sub> SO <sub>4</sub>	Approximate Normality.
1.032	5	N
1.059	9	2N
1.087	13	3N
1.178	25	6N
1.285	38	10N
1.404	51	14N
1.831	94	35N

TABLE 1 D.

S. G. of Aqueous Acetic Acid Solution. at 20°/4° C.		
S. G.	Per Cent HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	Approximate Normality
1.015	12	2N
1.044	35	6N
1.050	42	7N
1.062	57	10N
1.070	79	14N
1.050	100	17.5N

TABLE 2.

S. G. of Aqueous Ammonium Hydroxide Solutions at 20°/4° C.

S. G.	%NH <sub>3</sub>	Approximate Normality
0.957	10	6
0.922	20	11
0.908	25	14
0.900	28.3	15
0.892	80	16

TABLE 3 A.  
Clark's Table of Hardness of Water.  
( in Degrees )

ml.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	—							0.00	0.11	0.22
1	0.33	0.44	0.55	0.67	0.78	0.89	1.00	1.09	1.18	1.27
2	1.36	1.45	1.54	1.64	1.73	1.83	1.93	2.01	2.09	2.18
3	2.28	2.37	2.46	2.55	2.64	2.73	2.82	2.91	3.00	3.10
4	3.20	3.30	3.40	3.50	3.60	3.70	3.80	3.90	4.00	4.10
5	4.20	4.30	4.40	4.50	4.60	4.70	4.80	4.90	5.00	5.10
6	5.20	5.30	5.40	5.50	5.60	5.70	5.80	5.90	6.00	6.10
7	6.30	6.30	6.40	6.50	6.60	6.70	6.80	6.90	7.00	7.10
8	7.21	7.32	7.42	7.53	7.63	7.74	7.84	7.94	8.05	8.16
9	8.26	8.37	8.48	8.58	8.69	8.79	8.90	9.00	9.11	9.21
10	9.32	9.42	9.53	9.63	9.74	9.84	9.95	10.06	10.16	10.28
11	10.39	10.50	10.61	10.72	10.83	10.94	11.05	11.17	11.28	11.39
12	11.50	11.61	11.72	11.83	11.94	12.05	12.17	12.28	12.39	12.50
13	12.61	12.72	12.83	12.94	13.06	13.17	13.28	13.39	13.50	13.61
14	13.72	13.83	13.94	14.06	14.17	14.28	14.39	14.50	14.61	14.72
15	14.83	14.95	15.06	15.18	15.29	15.41	15.53	15.65	15.76	15.88
16	16.00									

TABLE 3 B.

Substance	Solubility per 100 gms. of water at 0°C
CaO	0.13
CaCO <sub>3</sub>	0.0036
MgCO <sub>3</sub>	0.01
CaSO <sub>4</sub>	0.18
MgSO <sub>4</sub>	24.70
Na <sub>2</sub> CO <sub>3</sub>	7.00

TABLE 3 C.

Hardness-causing salts in grains per Imperial gallon of water from the sources indicated.

	1.	2.	3.
CaCO <sub>3</sub>	6.96	12.98	3.32
MgCO <sub>3</sub>	nil	8.13	trace
CaSO <sub>4</sub>	nil	nil	93.21
MgSO <sub>4</sub>	nil	nil	144.62
MgCl <sub>2</sub>	nil	nil	220.55
NaCl	0.90	0.20	1850.74
SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , etc.	1.09	2.04	trace

1. Water from the Ganges (drawn from the University ghat in January) 2. From a Well on the University grounds.  
3. Sea water.



TABLE 4.

Analyses of Typical Indian Iron ores.

Constituents	1	2	3	4 *
Insoluble Matter	—	—	—	—
SiO <sub>2</sub>	0.91	5.11	1.11	43.00
Fe <sub>2</sub> O <sub>3</sub>	94.22	×	×	—
FeO	0.47	×	×	—
Total Iron	66.30	59.36	63.90	36.20
Al <sub>2</sub> O <sub>3</sub>	0.98	4.52	1.40	1.80
TiO <sub>2</sub>	trace	×	trace	nil
MnO	0.18	0.60	trace	nil
CaO	0.26	×	×	2.08
MgO	trace	×	×	1.91
P <sub>2</sub> O <sub>5</sub>	0.072	0.144	0.069	0.18
S	trace	×	trace	×
H <sub>2</sub> O + organic matter }	2.65	×	5.40	×

× This mark denotes 'not determined'. \* Magnetite from Sa'lem, S. India.

TABLE 5.

	1	2	3	4
Insoluble } Matter }	×	3.58	2.93	1.61
SiO <sub>2</sub>	3.54	×	0.99	×
Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub>	4.06	1.43	0.77	0.73
CaO	29.00	29.69	52.64	2.03
MgO	18.11	20.03	1.42	45.25
Loss on } Ignition }	×	×	41.62	50.34

1 and 2. Dolomite. 3. Limestone. 4. Magnesite.

× This mark denotes 'not determined.'

TABLE 6.

	Portland Cement.	Alumina Cement
	Per Cent	Per Cent
SiO <sub>2</sub>	23.56	9.56
Fe <sub>2</sub> O <sub>3</sub>	2.46	8.05
Al <sub>2</sub> O <sub>3</sub>	7.50	42.15
CaO	62.02	32.30
MgO	2.50	
SO <sub>2</sub>	1.50	
Loss on ignition	0.46	
TiO <sub>2</sub>		7.94

TABLE 7.

Percentage composition of Indian Pig Iron Grades.  
 Grade nos. 1 to 5 from B. F. using coke 5 Basic, 6 from B. F.  
 using charcoal, (all grades)

	2		3		4		5	
Si	2.75 to 3.25	2.25 to 2.25	1.75 to 2.25	1.50 to 1.75	1.00 to 1.25	0.50 to 2.75		
S	<0.035	<0.05	<0.05	<0.05	<0.05	<0.05	0.02	
P	<0.400	<0.40	<0.0	<0.40	<0.35	0.10		
Mn	1.00 to 1.50	1.00 to 1.50	1.00 to 1.50	1.00 to 1.50	1.00 to 1.50	0.4 to 0.80		
T. C.	3.70 to 4.20	3.70 to 4.20	3.70 to 4.20	3.70 to 4.20	3.70 to 4.20	3.70 to 4.20		
G. C.	3.00 to 3.50	3.00 to 3.50	3.00 to 3.20	3.00 to 3.20	2.00 to 3.00	3.00 to 3.50		
U. C.	0.30 to 0.70	0.30 to 0.70	0.30 to 0.70	0.30 to 0.70	1.20 to 1.70	0.30 to 0.70		

## Low Manganese Basic Pig

## High Manganese Basic Pig

Si	1.00 to 1.25.	1.00 and under
S	Under 0.05	Under 0.05
P	Under 0.35	Under 0.35
Mn	0.50 to 1.00	1.50 to 1.75

TABLE 8 A.

Typical composition of Steels for different uses.

	Soft for Sheets&plates	Mild steel for Structures	Rail Steel	Chrome Steel forRail	High Tensile Structuralsteel
Carbon	0.10 to 0.15	0.20 to 0.30	0.45-0.68	0.42-0.53	Not <0.30
Silicon	—	0.28	0.05	Not <0.05	0.20
Sulphur	0.05	0.05	<0.05	Not <0.05	Not <0.05
Phosphorus	0.25	0.05	<0.05	Not <0.05	Not <0.05
Manganese	0.25 to 0.60	0.50 to 0.60	0.60 to 0.90	0.65 to 0.85	0.50 to 1.30
Chromium	—	—	—	0.75 to 1.00	0.50 to 1.10

TABLE 9.

1 and 2 Ferro-manganese and 3 Spiegel.

	1	2.	3
Si	1.51	2.35	1.74
S	0.022	0.025	0.020
P	1.75	0.55	0.020
Mn	66.00	73.50	26.75
C	5.95	5.90	5.50

TABLE 10.

## Manganese ore

SiO <sub>2</sub>	6.63
Fe	5.89
Mn	51.61
P	0.091

TABLE 11 A.

	1. Copper ore.	2. Concentrate.	3. Matte.
	1.	2.	3.
Insoluble Matter }	64.50	5.34	×
Cu	2.20	30.90	39.50
Fe	11.25	29.40	41.50
Ni	0.191	×	×
S	×	32.92	×

× This mark indicates 'not determined'.

## 1. Dump Slag and 2. Refinery Slag. ( Copper Smelting )

	1.	2
Cu	0.22	31.65
Fe	×	6.30
Ni	×	1.25
CaO	×	0.15
SiO <sub>2</sub>	×	55.00

× This mark denotes 'not determined'.

TABLE 12

## Lead Smelting ores.

Constituents	1	2	3	4
	Per Cent.			
ozs. Silver per ton	19.6	14.5	30.1	10.0
Lead	23.2	10.6	39.8	13.1
Zinc	12.8	5.5	14.8	14.5
Copper	0.4	4.9	0.4	0.7
Iron	4.1	8.8	4.3	4.3

Silica	×	44.6	17.8	×
Alumina	×	×	×	×
Calcium oxide	×	3.7	×	×
Magnesia	×	×	×	×
Sulphur	×	11.0	16.0	×
Lead monoxide	0.3	—	—	1.9

1. Ore for concentration. 2. Copper-lead ore. 3. High grade lead ore. 4. Gossan ore.

× This mark denotes 'not determined'.

TABLE 13.

1. Coarse concentrate (Wilfley Table) 2. Flotation concentrate.  
3 Pot sinter.

	1	2	3
Ounces } Silver } Per ton }	45.00	41.00	35.00
	Per Cent		
Pb	66.00	69.00	53.09
Zn	8.50	7.53	10.40
Cu	0.40	0.60	0.50
Fe	3.00	1.50	14.00
SiO <sub>2</sub>	1.40	1.20	6.80
S	18.00	17.50	2.40
H <sub>2</sub> O	2.60	6.10	—
CaO	—	—	3.6

TABLE 14.

1. Copper matte. 2. Copper-Nickel speiss.

	Per Cent	
Constituents	1	2
Ni	—	32.88
Cu	40.40	9.05
Pb	28.60	2.75
Ag ( ozs. Per ton )	59.9	24.40
As....	—	34.76
Sb....	—	5.00
Fe....	—	10.25

TABLE 14 A\*

1. Ore feed to the mills.
2. Lead concentrate.
3. Zinc concentrate.

Constituents	Per Cent.		
	1	2	3
Lead	10.0	70.0	3.5
Zinc	6.0	3.7	51.0
Copper	0.1	0.2	0.1
Sulphur	28.0	17.0	33.0
Iron	35.0	7.0	11.0
ozs Silver per ton }	4.0	26.0	2.0

\* Through the courtesy of Prof N. P. Gandhi, who visited the plant of the Consolidated Mining Co. Ltd. at Trail ( British Columbia ) in 1938.

TABLE 15.

1. Iron Blast Furnace Slag (Coke)
2. " " " " (Charcoal)
3. Basic Open hearth Slag
4. Electric Steel Furnace Slag.

	1.	2	3	4
	Per Cent			
SiO <sub>2</sub>	26.72	41.00	17.26	22.66
FeO	1.48	x	9.54	23.48
Fe <sub>2</sub> O <sub>3</sub>	nil	{ 21.04	3.71	x
Al <sub>2</sub> O <sub>3</sub>	20.84		1.96	x
CaO	30.11	26.78	26.78	26.00
MgO	19.61	7.24	4.94	4.94
MnO	0.80	2.19	8.89	x
TiO <sub>2</sub>	x	x	0.73	x
SO <sub>3</sub>	x	x	0.30	x
P <sub>2</sub> O <sub>5</sub>	x	x	4.20	4.98
S	x	x	x	x

x This mark denotes 'not determined.'

1. White Fire-clay for brick laying. 2. Black clay. 3. Silica Brick. 4. Mica schist. 5. Chrome Brick. 6. Chromite. 7. Magnesite Brick.

Per Cent.

Constituents	1	2	3	4	5	6	7
SiO <sub>2</sub>	62.12	53.96	92.64	91.32	9.28	4.78	3.89
Fe <sub>2</sub> O <sub>3</sub>	1.86	2.60	0.57	0.29	—	—	4.17
FeO	—	—	—	—	21.98	22.19	—
Al <sub>2</sub> O <sub>3</sub>	22.80	28.78	1.23	6.43	11.74	8.95	1.08
MnO	trace	trace	nil	nil	nil	0.23	—
TiO <sub>2</sub>	1.96	1.02	nil	nil	nil	nil	—
CaO	1.55	0.55	1.90	0.10	0.40	0.95	6.02
MgO	0.42	trace	1.03	0.14	12.10	12.67	85.15
Cr <sub>2</sub> O <sub>3</sub>	—	—	—	—	44.05	47.64	—
Total alkalis.	0.34	1.74	0.24	0.10	—	—	—
Loss on Ignition.	9.42	11.90	1.50	0.90	0.96	1.50	0.18
SO <sub>3</sub>	—	—	—	—	—	0.06	—

\* Proceedings of the Empire Mining and Metallurgical Congress, 1927.

TABLE 17.

Analyses of clays used for making moulds for brass pots.

	1	2
	Per Cent.	
Silica	60.40	66.00
Ferric oxide	2.63	2.02
Alumina	24.20	23.20
Calcium oxide	1.40	1.81
Magnesium oxide	2.87	3.92
Loss on Ignition	7.62	3.25

TABLE 18.

Bauxite.

1. From the Central Provinces. 2. From Kolhapur State.

	Per Cent	
	1	2
Silica	3.00	5.56
Ferric oxide	5.10	7.30

Alumina	54.96	66.49
Titania	9.24	5.20
Calcium oxide	×	0.28
Magnesia	×	3.80
Loss on } Ignition }	25.00	11.37

× This denotes 'not determined.'

TABLE 18 A.

## Felspar.

Constituents	Per Cent.	
	1	2
SiO <sub>2</sub>	65.02	55.44
Fe <sub>2</sub> O <sub>3</sub>	0.61	Trace
Al <sub>2</sub> O <sub>3</sub>	13.82	10.14
CaO	0.10	0.90
MgO	0.76	0.14
Na <sub>2</sub> O	2.26	1.87
K <sub>2</sub> O	8.02	12.01

1. Source Unknown. 2. Ramgarh.

TABLE 19.

## Type Metal

1. Monotype. 2. 'Fry'

	Per Cent.	
	1	2
Lead	82.14	79.90
Antimony	12.30	13.75
Tin	4.04	4.50
Copper	0.09	×

× This mark denotes 'not determined'

TABLE 20.

## Phosphor Bronze.

Constituents	Per Cent	
	1	2
Tin	9.50	10.85
Zinc	1.80	4.64
Lead	1.95	3.74
Phosphorus	0.38	0.09
Copper	86.27	80.64

TABLE 21.

Alsimin	
Constituents	Per Cent
Carbon	0.80
Silicon	34.94
Iron	9.00
Aluminium	54.98
Manganese	0.12
Titanium	0.18

TABLE 22.

Ferro-Silicon	
	Per Cent
Iron	16.90
Silicon	80.33

TABLE 23.

Ferro-tungsten	
	Per Cent
Carbon	0.04
Tungsten	79.33

TABLE 24.

Ferro-phosphorus	
	Per Cent
Silicon	1.98
Iron	70.60
Phosphorus	25.30

TABLE 25.

Ferro-molybdenum	
	Per Cent
Carbon	0.30
Silicon	1.42
Iron	32.70
Molybdenum	65.20



TABLE 26.

## Ferro-chrome

	Per Cent
Carbon	5.50
Iron	27.10
Chromium	65.50

TABLE 27.

## Ferro-vanadium

	Per Cent
Carbon	0.10
Vanadium	46.50

TABLE 28.

## Flue Dust ( Iron Blast Furnace )

	Per Cent
$\text{SiO}_2$	13.13
$\text{Fe}_2\text{O}_3$	23.00
$\text{Al}_2\text{O}_3$	6.68
$\text{CaO}$	7.45
$\text{MgO}$	4.71
S	0.51
$\text{P}_2\text{O}_5$	0.26
$\text{TiO}_2$	0.34
Loss on ignition }	42.52

TABLE 29 A\*

## Tungsten-Chromium Steel

	Per Cent
Tungsten	6.68
Chromium	1.46

\* Sample supplied by the Hukumchand Electric Steel Works  
Calcutta.

TABLE 29\*

## Railway Materials

1. Carbon Spring steel. 2. Carbon Spring steel with special Silicon Requirements. 3. Chrome-Vanadium Spring steel. 4. Silico-Manganese spring steel. 5. Axles for Railway Carriages. 6. Axles for Locomotives. 7. Tyres for Railway carriage wheels.

	1	2	3	4	5	6	7
			Per Cent				
Carbon	0.90 to 1.10	0.90 to 1.05	0.50 to 0.60	0.55 to 0.65	0.40 to 0.55	0.25 to 0.70	0.50 to 0.85
Manganese	0.50	0.25 to 0.50	0.60 to 0.90	0.60 to 0.90	0.50 to 0.90	0.40 to 0.70	not > 0.75
Phosphorus	0.05	0.05	not > 0.045	< 0.054 not > 0.05	not > 0.05	not > 0.05	not > 0.05
Sulphur	0.05	0.05	not > 0.045	< 0.045 not > 0.06	not > 0.06	not > 0.05	not > 0.05
Silicon	—	0.15	—	1.80 to 2.20	—	1	0.15 to 0.35
Chromium	—	—	0.90— 1.10	—	—	—	—
Vanadium	—	—	not > 0.15	—	—	—	—

\*Extracted from the 1936 Edition of the Book of Standards (Vol. 1) of the American Society for Testing Materials,

TABLE 30

## Nickel Chromium Steel

	Per Cent
Nickel	3.21
Chromium	0.83
Carbon	0.25

TABLE 30A

## High Chromium Steel

(Heat resisting)

	Per Cent.
Silicon	1.114
Sulphur	0.032
Phosphorus	0.042
Manganese	0.28
Carbon	0.83
Chromium	25.84

TABLE 31

Fineness of Silver Coin  
( In Circulation before World War II. )

	Parts fine per thousand
Silver Coin	916.0

TABLE 32

Nickel Coin  
( In circulation before World War II. )

	Per Cent
Copper	75.00
Nickel	25.00

TABLE 32A

Bronze-, Copper coins )

	Per Cent
Copper	95.00
Tin	4.00
Zinc	1.00

TABLE 32 B.

( Current four anna coin )

Quaternary Alloy.

	Per Cent
Silver	49.68
Copper	39.74
Nickel	5.00
Zinc	5.20

TABLE 32 C.

Current half-anna coin.

Copper	79.02
Nickel	1.00
Zinc	20.00

TABLE 33

Platinum-gold Alloy

	Per Cent	Parts fine per thousand
Platinum	5.46	54.60
Gold	61.54	615.4

TABLE 33A.

## Duralumin

1. British Standards Institution Specification for Duralumin for aeronautical purposes. 2, 3, 4 are samples (rods 0.75" dia. ) analysed in the Lab of the Dept. of Min. and Met.

	1	2	3	4
Copper	not < 3.5 and not > 4.5	3.75	3.34	4.30
Manganese	„ < 0.4 „ > 0.7	0.35	0.26	0.31
Magnesium	„ < 0.4 „ > 0.7	0.40	0.50	0.35
Silicon	not > 0.7	0.28	0.21	0.26
Iron	not > 0.7	0.17	0.26	0.34
Titanium	not > 0.3	x	x	x
Aluminium	the remainder	x	x	

x This mark indicates 'not determined'.

TABLE 34\*

## Nickel Cobalt ore from Nepal.

Per Cent.

Insoluble Matter	31.05
Ferric Oxide	2.91
Alumina	0.55
Nickel	0.36
Cobalt	8.74
Arsenic	7.69
Calcium Oxide	13.85
Magnesium Oxide	9.60
Sulphur	3.66
Carbon di Oxide	21.84

\* Sample supplied thorough the courtesy of Mr. Sharma, Bombay.

TABLE 34 A

## Zinc Blende.

Per Cent.

Zinc	45.36
Iron	3.01
Manganese	0.62
Calcium oxide	15.63
Sulphur	21.31
Insoluble } Matter }	0.31
Loss on Ignition	33.40

TABLE 34 B

## Zinc Dross

	Per Cent.
Silicon	Trace
Pb	1.12
Cu	Trace
Fe	4.10
Al	0.65
Zn	93.95

TABLE 34 C

## Zinc Ash

( Dry Basis )

	Per Cent
SiO <sub>2</sub>	2.35
Fe	2.42
Al	0.58
Zn	76.00
Pb	2.97
Cl <sub>2</sub>	1.72
O <sub>2</sub>	13.96

TABLE 34 D

## Flux Skimmings

	Per Cent
Insolubles	0.62
Fe <sub>2</sub> O <sub>3</sub>	0.83
Al <sub>2</sub> O <sub>3</sub>	0.37
NH <sub>4</sub> Cl	12.03
ZnCl <sub>2</sub>	29.30
ZnO . .	52.47
Zn ( Calculated )	56.94

TABLE 35\*

Samples of Beryl from Nellore Dis rict.

		Per Cent.	
		1	2
Silica	SiO <sub>2</sub>	67.28	64.78
Alumina	Al <sub>2</sub> O <sub>3</sub>	6.10	16.56
Ferric Oxide	Fe <sub>2</sub> O <sub>3</sub>	0.43	1.99
Beryllium Oxide	BeO	13.51	13.53
Calcium Oxide	CaO	0.48	0.52
Potassium Oxide	K <sub>2</sub> O	—	—
Sodium Oxide	Na <sub>2</sub> O	0.64	0.56
Lithium Oxide	Li <sub>2</sub> O	Trace	Trace
Water	H <sub>2</sub> O	1.60	2.10

\* Trans., Geo. &amp; Min. Insti., Vol. 22, Pt. 3., Oct. 1928.

TABLE 35 A.

Copper-Beryllium Alloy.

	Per Cent
Beryllium	3.01
Copper	not determined.

TABLE 36.

Proximate Analysis of coal from the Jharia field.

As received.		Air Dry.
Per Cent		Per Cent
Volatile } Matter }	19.2	19.3
Fixed Carbon	63.2	63.6
Moisture	2.0	1.4
Ash	15.6	15.7
Colour of } Ash }	Brownish white	Brownish white

TABLE 36 A.

Ultimate Analysis of coal from the Jharia field.

	As received. Per Cent	Air Dry Per Cent
Carbon	68.18	68.60
Hydrogen	4.52	4.60
Oxygen } Nitrogen }	8.99	9.05
Sulphur	0.60	0.60
Phosphorus	0.06	0.06
Moisture	2.00	1.40
Ash	15.60	15.70

TABLE 37.

Proximate Analysis of coal from the Raneegunj field.

	As received. Per cent	Air dried. Per cent.
Volatile Matter	33.8	34.2
Fixed Carbon	51.9	52.4
Moisture	2.4	1.4
Ash	11.9	12.0
Colour of Ash.	Light brown	Light brown

TABLE 37 A.

Ultimate Analysis of the coal sample shown in Table 37.

	As received. Per cent.	Air dried Per Cent.
Carbon	69.82	70.55
Hydrogen	4.06	4.10
Oxygen and } Nitrogen }	11.26	11.37
Sulphur	0.51	0.52
Phosphorus	0.06	0.06
Moisture	2.40	1.40
Ash. .	11.88	12.00

TABLE 38.

Proximate Analysis of coal from the Giridih field.

(Moisture-free basis)

	Per Cent.
Volatile Matter	26.90
Fixed Carbon	59.20
Ash	13.50
Sulphur	0.39

TABLE 39.

	J	R	A	G
Calorific Value	7010	6940	7220	7420
(gm-calories)				
Evaporative } Power }	13.1	12.8	13.40	13.9
Caking Index	8	5	6	12.0
Yield of Tar } in lbs. per ton of coal }	145.3	×	×	×
Yield of liquor } in lbs. per ton of coal }	51.7	×	×	×
Yield of gas in } c. ft. per ton of coal }	10,180	×	×	×
S. G. of coal } (Apparent.) }	1.45	1.42	1.27	1.34
J denotes	Sample from the Jharia field			
R „	Ranigunj „			
A „	Assam „			
G „	Giridih „			

× This mark denotes 'not determined'.



TABLE 39 A

## COAL—TAR

S. G. at 15°C. 1.21

Ammoniacal	}	Per cent
Liquor		2.0
Distillate		
up to 170°C.		3.0
Between 170°-230°C.		4.5
„ 230- 70°C.		11.5
270°-350°C.		23.5
Pitch		55.5
Naphthalene		9.5
Viscosity	}	5
( Hutchinson )		seconds

TABLE 40

## Ammonium Sulphate

	Per Cent
Moisture	0.60
Acidity ( Free sulphuric acid )	0.39
Ammonia	25.25
Ammonium Sulphate	98.40

TABLE 41

1. Coke oven gas.		2. Producer gas.	
Constituents	1	Per Cent	2
CO <sub>2</sub>	2.5		5.9
Cx Hy	30		—
O <sub>2</sub>	0.5		0.3
CO	8.5		25.9
CH <sub>4</sub>	26.5		3.5
H <sub>2</sub>	46.5		13.2
N <sub>2</sub> ( By difference )	12.5		51.2
Calorific			
Value in B. Th. U.	}	540	161.5
per cu. ft. at N. T. P.			

TABLE 42

## Petrol

S. G. at 30°C/30°C.	Not above 0.752
Iodine Value	Not more than 7.0 C/o-101/5.

TABLE 43

Kerosene, first quality, for wick lamps.

Closed flash-point ( Abel-Pensky )	} Not below 38°C.
Sulphur	
	Not more than 0.061%

TABLE 44

Kerosene, Second Quality, for use in pressure lamps,  
stoves, blow lamps and oil engines.

Closed flash-point ( Abel-Pensky )	Not less than 40°C.
---------------------------------------	---------------------

TABLE 45

Fuel oil for internal combustion engines such as diesel semi-  
diesel and crude oil engines.

Closed flash-point.	
( Gray or Pensky-Martens )	Not below 65°C.
Viscosity at 40°C. (Redwood)	Not above 150 seconds.
Ash	Not > 0.05%
Sulphur	Not > 3.00%

TABLE 46.

Compounded cylinder oil for Cylinders of condensing  
engines and locomotives using superheated steam at temp. ex-  
ceeding about 500°F.

Approved fatty oil	5.0%
S. G. at 30°C. /33°C.	Not above 0.900
Viscosity ( Redwood ) at 100°C.	over 50 seconds.
Closed flash-point	Not below 280°C.
Ash	Not more than 0.05%

TABLE 47.

Fuel oil for oil-fired furnaces.

Closed flash-point	Not below 65°C.
Viscosity at 40°C. ( Redwood. )	Not above 200 seconds.
Ash	Not more than 0.2%

TABLE 48.

Compounded Cylinder oil for cylinders of condensing engines and locomotives using saturated steam and superheated steam at temp. not exceeding 500° F.

Approved fatty oil	5%
S. G. at 30°C./30°C.	Not above 0.900
Viscosity at 100°C. (Redwood)	110 to 150 seconds
Closed flash-point (Gray or Pensky Martens) }	Not below 250°C.
Ash	Not more than 0.05%

TABLE 49\*

Govt. Specification for Castor oil.

S. G. at 30°C./30°C.	0.952-0.956
Saponification Value	178-184
Iodine Value	82-90
Acid Value	Not more than 6.0

Note :—Acid value is the number of milligrams of potassium hydroxide required to neutralise the free acid in one gram of the oil.

TABLE—50.

Requirements for Sieve Openings and Wire  
Diameters with Permissible variations.

Designation.	Corresponding U. S. Standard Sieve Series Number	Sieve opening		Wire Diameter.	
		mm.	in.	mm.	in.
1.	2.	3.	4.	5.	6.
4760 micron.	4	4.76	0.187	1.27	0.050
4000 " "	5	4.00	0.157	1.12	0.044
3360 " "	6	3.36	0.132	1.02	0.040
2830 " "	7	2.83	0.111	0.92	0.036
2380 " "	8	2.38	0.0937	0.84	0.0331
2000 " "	10	2.00	0.0787	0.76	0.0299
1680 " "	12	1.68	0.0661	0.69	0.0272
1410 " "	14	1.41	0.0555	0.61	0.0240
1190 " "	16	1.19	0.0469	0.54	0.0213
1000 " "	18	1.00	0.0394	0.48	0.0189
840 " "	20	0.84	0.0331	0.42	0.0165
710 " "	25	0.71	0.0280	0.37	0.0146
590 " "	30	0.59	0.0232	0.33	0.0130
500 " "	35	0.50	0.0197	0.29	0.0114
420 " "	40	0.42	0.0165	0.25	0.0098
350 " "	45	0.35	0.0138	0.22	0.0087
297 " "	50	0.297	0.0117	0.188	0.0074
250 " "	60	0.250	0.0098	0.162	0.0064
210 " "	70	0.210	0.0083	0.140	0.0055
177 " "	80	0.177	0.0070	0.119	0.0047
149 " "	100	0.149	0.0059	0.102	0.0040
125 " "	120	0.125	0.0049	0.086	0.0034
105 " "	140	0.105	0.0041	0.074	0.0029
88 " "	170	0.088	0.0035	0.063	0.0025
74 " "	200	0.074	0.0029	0.053	0.0021
62 " "	230	0.062	0.0024	0.046	0.0018
53 " "	270	0.053	0.0021	0.041	0.0016
44 " "	325	0.044	0.0017	0.036	0.0014

Note:—Sieves having larger openings than those included in the table may be specified, but in specifying sieves of larger openings the actual size of the opening (in millimeters or in inches) shall be stated. A tolerance of 3 per cent on average openings and of 10 percent in maximum openings shall be permitted.

Tolerance in Average opening,	Tolerance on Wire Diameter, per cent.		Tolerance in Maximum opening, per cent
7.	8.	9.	10.
± 3	15	30	10
± 3	15	30	10
± 3	15	30	10
± 3	15	30	10
± 3	15	30	10
± 3	15	30	10
± 3	15	30	10
± 3	15	30	10
± 3	15	30	10
± 3	15	30	10
± 5	15	30	25
± 5	15	30	25
± 5	15	30	25
± 5	15	30	25
± 5	15	30	25
± 5	15	30	25
± 5	15	30	25
± 6	15	35	40
± 6	15	35	40
± 6	15	35	40
± 6	15	35	40
± 6	15	35	40
± 6	15	35	40
± 6	15	35	40
± 8	15	35	60
± 8	15	35	60
± 8	15	35	60
± 8	15	35	60
± 8	15	35	60
± 8	15	35	60

TABLE 51.

Institution of Mining and Metallurgy Standard Sieves.

Mesh or Aperture per linear inch.	Diameter of wire.		Aperture		Screening area.
	Inch.	mm.	Inch.	mm.	Percent.
5	0.1	2.540	0.1	2.540	25.0
8	0.063	1.600	0.062	1.574	24.6
10	0.05	1.270	0.05	1.270	25.0
20	0.025	0.635	0.025	0.635	25.0
30	0.0167	0.424	0.0166	0.421	24.8
60	0.0083	0.211	0.0083	0.211	24.8
90	0.0055	0.139	0.0054	0.139	24.5
100	0.005	0.127	0.005	0.127	25.0
120	0.0041	0.104	0.0042	0.107	25.4
150	0.0033	0.084	0.0033	0.084	24.5
200	0.0025	0.063	0.0025	0.063	25.0

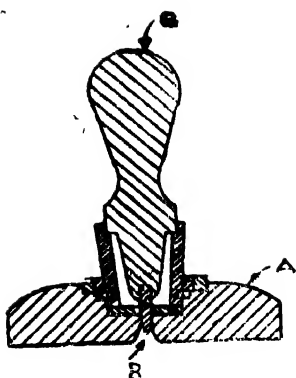


Fig. 22 To face p. 406.

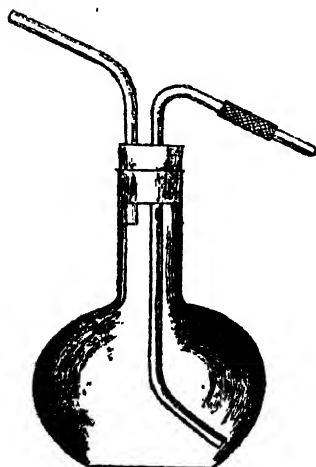


Fig. 2 To face. p. 12.

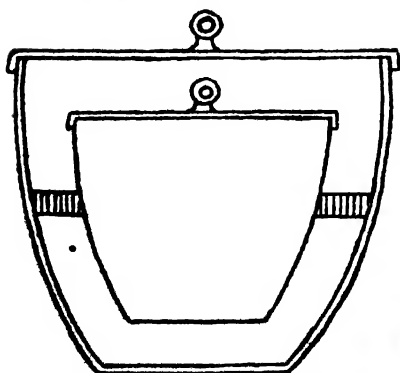


Fig. 17a To face pp. 237, 362.

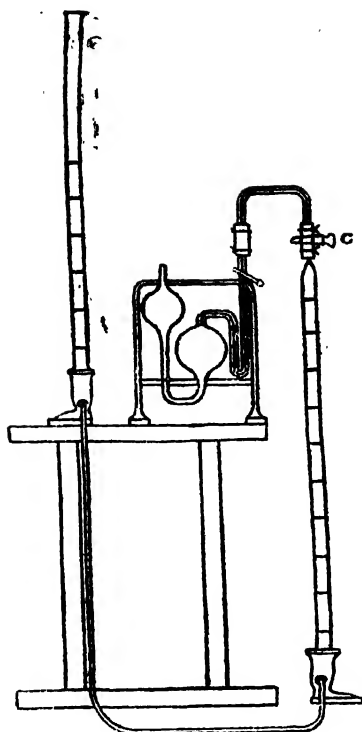


Fig. 34f. To face p. 498.

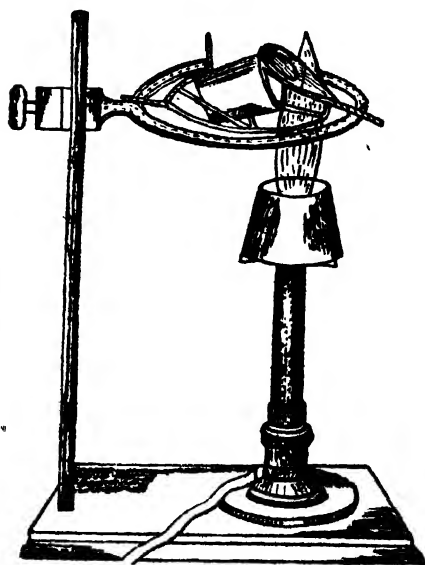


Fig. 5. To face p. 19.

Soda-lime guard tube.

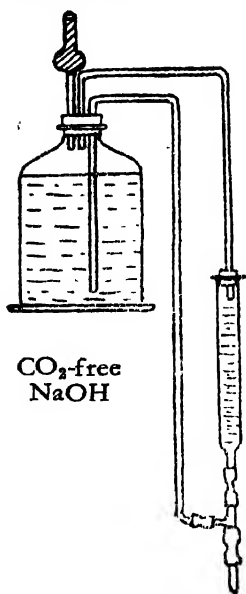


Fig. 36a. To face p. 493

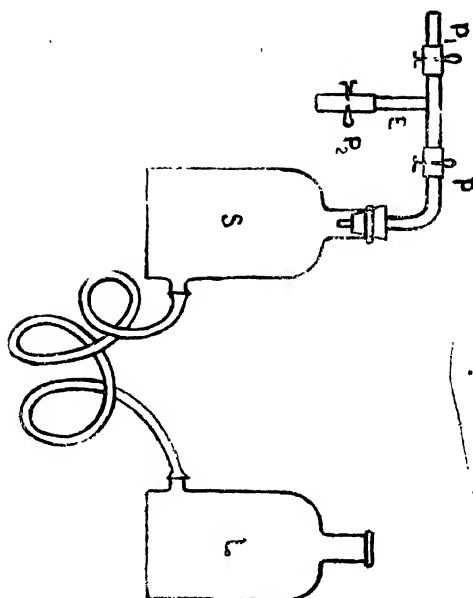


Fig. 4. To face p. 88.



Fig. 2b. To face p. 20.

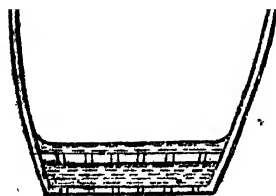
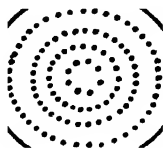


Fig. 24. To face p. 19.

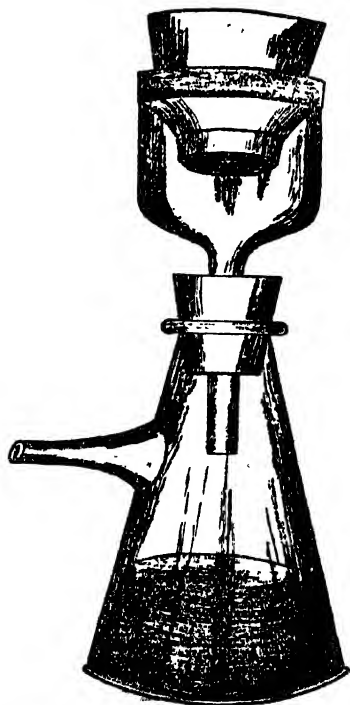


Fig. 11a. To face pp. 156, 416.

## USEFUL CONSTANTS.

1 Inch = 25·40 millimetres. 1 mm. = ·03937 inch.

1 Gallon = ·1604 cubic foot = 10 lb. of water at 62° F.

1 Knot = 6080 feet per hour = 1 Nautical mile per hour.

Weight of 1 lb. in London = 445,000 dynes.

One pound avoirdupois = 7000 grains = 453·6 grammes.

1 Cubic foot of water weighs 62·3 lb.

1 Cubic foot of air at 0° C. and 1 atmosphere, weighs ·0807 lb.

1 Cubic foot of Hydrogen at 0° C. and 1 atmosphere, weighs ·00559 lb.

1 Foot-pound =  $1·3562 \times 10^7$  ergs.

1 Horse-power-hour =  $33000 \times 60$  foot-pounds.

1 Electrical unit = 1000 watt-hours = 1·34 horse-power-hours.

Joule's Equivalent is  $\left\{ \begin{array}{l} 773 \text{ ft.-lb.} = 1 \text{ Fah. unit.} \\ 1400 \text{ ft.-lb.} = 1 \text{ Cent. } \end{array} \right.$

1 Horse-power = 33000 foot-pounds per minute = 746 watts.

Volts  $\times$  amperes = watts.

1 Atmosphere = 14·7 lb. per square inch = 2116 lb. per square foot =

760 mm. of mercury =  $10^6$  dynes per sq. cm. nearly.

A column of water 2·3 feet high corresponds to a pressure of 1 lb.  
per sq. inch.

Absolute temp.,  $t = \text{° C.} + 273^0$  or  $\text{° F.} + 459·4^0$ .

One radian = 57·30 degrees.

To convert common into Napierian logarithms, multiply by 2·3026.

The base of the Napierian logarithms is  $e = 2·7183$ .

The value of  $g$  at London = 32·182 feet per sec. per sec.





## LOGARITHMS.

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	9	13	17	21	26	30	34	38
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	12	16	20	24	28	32	37
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	11	14	18	21	25	28	32
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	7	10	14	17	20	24	27	31
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	7	10	13	16	20	23	26	30
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	9	11	14	17	20	23	26
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	14	16	19	22	25
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	3	5	8	10	13	15	18	21	23
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	6	8	11	13	15	17	19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	2	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8

## LOGARITHMS.

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	2	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	4	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	4	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9913	9917	9922	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	4	4

## ANTILOGARITHMS.

					6	7	8	9	1	2	3	4	5	6	7	8	9		
00	1000	002	1005	1007	1009	112	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
01	1023	026	1028	1030	1033	135	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
02	1047	050	1052	1054	057	059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
03	1072	074	1076	1079	081	084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
04	1096	099	1102	1104	107	109	1112	1114	1117	1119	0	1	1	1	1	1	2	2	2
05	1122	125	1127	1130	132	135	1138	1140	1143	1146	0	1	1	1	1	1	2	2	2
06	1148	151	1153	1156	159	161	164	1167	1169	1172	0	1	1	1	1	1	2	2	2
07	1175	178	1180	1183	186	189	191	1194	1197	1199	0	1	1	1	1	1	2	2	2
08	1202	205	1208	1211	213	216	219	1222	1225	1227	0	1	1	1	1	1	2	2	2
09	1230	233	1236	1239	242	245	247	1250	1253	1256	0	1	1	1	1	1	2	2	2
10	1259	262	1265	1268	271	274	276	1279	1282	1285	0	1	1	1	1	1	2	2	2
11	1288	291	1294	1297	300	303	306	1309	1312	1315	0	1	1	1	1	2	2	2	2
12	1318	321	1324	1327	1330	334	337	1340	1343	1346	0	1	1	1	1	2	2	2	2
13	1349	352	1355	1358	361	365	368	1371	1374	1377	0	1	1	1	1	2	2	2	2
14	1380	384	1387	1390	393	396	400	1403	1406	1409	0	1	1	1	1	2	2	2	2
15	1413	416	1419	1422	426	429	432	1435	1439	1442	0	1	1	1	1	2	2	2	2
16	1445	449	1452	1455	456	462	466	1472	1476	1479	0	1	1	1	1	2	2	2	2
17	1479	483	1486	1489	493	496	500	1503	1507	1510	0	1	1	1	1	2	2	2	2
18	1514	517	1521	1524	528	531	535	1538	1542	1545	0	1	1	1	1	2	2	2	2
19	1549	552	1556	1560	563	567	570	1574	1578	1581	0	1	1	1	1	2	2	2	2
20	1585	589	1592	1596	1600	603	607	1611	1614	1618	1	1	1	1	2	2	2	2	2
21	1622	626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	2	2	2
22	1660	663	1667	1671	1675	1679	683	1687	1690	1694	0	1	1	2	2	2	2	2	2
23	1698	702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	2	2	2
24	1738	742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	2	2	2
25	1778	782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	2	2	2
26	1820	824	1828	1832	1836	1841	1845	1849	1854	1858	0	1	1	2	2	2	2	2	2
27	1862	866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	2	2	2	2
28	1905	910	1914	1918	1923	1928	1932	1936	1941	1945	0	1	1	2	2	2	2	2	2
29	1950	954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	2	2	2	2
30	1995	2000	2004	2009	2013	2018	2023	2028	2032	2037	0	1	1	2	2	2	2	2	2
31	2042	2046	2051	2056	2060	2065	2070	2075	2080	2084	0	1	1	2	2	2	2	2	2
	2089	2094	2099	2104	2108	2113	2118	2123	2128	2133	0	1	1	2	2	2	2	2	2
	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	2	2	2	2
34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2233	1	1	2	2	2	2	2	2	2
	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	2	2	2	2	2
	2291	2296	2301	2307	2312	2317	2323	2328	2333	2338	1	1	2	2	2	2	2	2	2
37	2344	2350	2355	2360	2365	2371	2377	2382	2388	2393	1	1	2	2	2	2	2	2	2
	2399	2404	2410	2415	2420	2427	2432	2438	2443	2448	1	1	2	2	2	2	2	2	2
38	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	2	2	2	2	2
	2512	2518	2523	2529	2535	2541	2547	2553	2559	2565	1	1	2	2	2	2	2	2	2
	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	2	2	2	2	2
	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	2	2	2	2	2
	2693	2698	2704	2710	2716	2722	2729	2735	2742	2748	1	1	2	2	2	2	2	2	2
	2755	2761	2767	2773	2779	2786	2793	2799	2805	2812	1	1	2	2	2	2	2	2	2
5	2818	2825	2831	2838	2844	2850	2858	2864	2871	2877	1	1	2	2	2	2	2	2	2
	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	2	2	2	2	2	2
	2951	2958	2965	2972	2979	2986	2992	2999	3006	3011	1	1	2	2	2	2	2	2	2
	3018	3027	3034	3041	3047	3053	3062	3069	3076	3081	1	1	2	2	2	2	2	2	2
	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	2	2	2	2	2	2

## ANTILOGARITHMS.

	0	1	2	3	4	5	6	7	8	9	1 2 3 4	5	6 7 8 9
50	8162	8170	8177	8184	8192	8199	8206	8214	8221	8228	1 1 2 8	4	4 5 6 7
51	8236	8243	8251	8258	8266	8273	8281	8289	8296	8304	1 2 2 8	4	5 5 6 7
52	8311	8319	8327	8334	8342	8350	8357	8365	8373	8381	1 2 2 8	4	5 5 6 7
53	8388	8396	8404	8412	8420	8428	8436	8443	8451	8459	1 2 2 8	4	5 6 6 7
54	8467	8475	8483	8491	8499	8508	8516	8524	8532	8540	1 2 2 8	4	5 6 6 7
55	8548	8556	8565	8573	8581	8589	8597	8606	8614	8622	1 2 2 8	4	5 6 7 7
56	8631	8639	8648	8656	8664	8673	8681	8690	8698	8707	1 2 3 8	4	5 6 7 8
57	8715	8724	8733	8741	8750	8758	8767	8776	8784	8793	1 2 3 8	4	5 6 7 8
58	8802	8811	8819	8828	8837	8846	8855	8864	8873	8882	1 2 3 4	4	5 6 7 8
59	8890	8899	8908	8917	8926	8936	8945	8954	8963	8972	1 2 3 4	5	5 6 7 8
60	8981	8990	8999	4009	4018	4027	4036	4046	4055	4064	1 2 3 4	5	6 6 7 8
61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1 2 3 4	5	6 7 8 9
62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1 2 3 4	5	6 7 8 9
63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1 2 3 4	5	6 7 8 9
64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1 2 3 4	5	6 7 8 9
65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1 2 3 4	5	6 7 8 9
66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1 2 3 4	5	6 7 9 10
67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1 2 3 4	5	7 8 9 10
68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1 2 3 4	6	7 8 9 10
69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1 2 3 5	6	7 8 9 10
70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1 2 4 5	6	7 8 9 11
71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1 2 4 5	6	7 8 10 11
72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1 2 4 5	6	7 9 10 11
73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1 3 4 5	6	8 9 10 11
74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1 3 4 5	6	8 9 10 12
75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1 3 4 5	7	8 9 10 12
76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1 3 4 5	7	8 9 11 12
77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1 3 4 5	7	8 10 11 12
78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1 3 4 6	7	8 10 11 13
79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1 3 4 6	7	9 10 11 13
80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1 3 4 6	7	9 10 12 13
81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2 3 5 6	8	9 11 12 14
82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2 3 5 6	8	9 11 12 14
83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2 3 5 6	8	9 11 13 14
84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2 3 5 6	8	10 11 13 15
85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2 3 5 7	8	10 12 13 15
86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2 3 5 7	8	10 12 13 15
87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2 3 5 7	9	10 12 14 16
88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2 4 5 7	9	11 12 14 16
89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2 4 5 7	9	11 13 14 16
90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2 4 6 7	9	11 13 15 17
91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2 4 6 8	9	11 13 15 17
92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2 4 6 8	10	12 14 15 17
93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2 4 6 8	10	12 14 16 18
94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2 4 6 8	10	12 14 16 18
95	8918	8938	8958	8978	8995	9016	9036	9057	9078	9099	2 4 6 8	10	12 15 17 19
96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2 4 6 8	11	13 15 17 19
97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2 4 7 9	11	13 15 17 20
98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2 4 7 9	11	13 16 18 20
99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2 5 7 9	11	14 16 18 20

## Appendix A.

### Common Laboratory Accidents and Remedies.

**Burns:**—Exclude air from the affected part by applying a thin paste of wheat or rice flour or by applying a little coconut oil, castor oil or vaseline. Picric acid gauze, i.e. gauze soaked in a solution of picric acid (1% strong) may be applied and held in position with a light bandage.

**Burns produced by acids or alkalis:**—Wash the part affected with a liberal quantity of water and then apply a mixture of raw linseed oil mixed with an equal volume of lime water. Such a mixture is known as carron oil. If the part affected is the eye and an acid is the reagent that has affected it, wash as quickly as possible with water and then with lime water. In the case of burns by alkalis, wash the affected part liberally with water and apply lemon juice or weak acetic acid. When the affected part is the eye, an additional wash with a saturated solution of boric acid is necessary. Castor oil dropped on the eye after the above treatment will have a soothing effect.

When strong acids are accidentally spilt on the Working-Bench, or on floor, sprinkle commercial sodium carbonate or lime and well mix with a glass rod. When effervescence has ceased on the addition of more of the soda or lime, wipe off with a duster and then sponge off with a wet duster.

**Cuts and wounds:**—Wash with clean cold water, remove pieces of glass or other foreign matter, dry, apply ammonia boric lint and bind up.

When chlorine or bromine vapour is inhaled, the remedy is to inhale ammonia from bottle containing ammonia solution or to moisten a handkerchief with rectified spirit and to inhale the alcohol vapour by holding the handkerchief near the nose.

When drops of strong acid have fallen on garments, rub at once with powdered ammonium carbonate or apply ammonia solution.

When drops of strong alkali have fallen on them, apply dilute acetic acid or lemon-juice. Wash with water or neutralize the excess of acid with ammonium carbonate solution.

The following is a tabular statement of the means whereby stains on garments and on the skin may be removed:—

Stain caused by	on garments.	on skin.
1. Pyrogalllic acid.	First moisten with ferrous sulphate solution (5%) and then wash with oxalic acid solution (5%). Give a final wash with water.	Dip the fingers into a solution of sodium sulphite (1 gm.) in 30 ml of water and 0.5 to 1 ml. of sulphuric acid s. g. 1.2, or the solution may be applied to the part stained.
2. Ferric chloride.	Wash with 10% oxalic acid solution in water.	Apply 10% oxalic acid solution to the part affected and then wash with water.
3. Black ink,	Rub with a tuft of cotton wool moistened with 10% oxalic acid solution. A final rub with bleaching powder is necessary.	Wash with ammonia solution of 0.96 s. g.
4. Red ink	Rub with a tuft of cotton wool soaked in hydrochloric acid of 1.05 s.g. and then wash with water.	Wash with soap and water.
5. Potassium Permanganate.	Rub with a tuft of cotton wool soaked in sulphurous acid solution, freshly made.	Rub with a tuft of cotton wool soaked either in a freshly made solution of sulphurous acid or in ferrous sulphate solution about 25% strong.

## Appendix B

The following is a list of the cupboard equipment issued to each student working in the Assay Laboratory of the College of Mining and Metallurgy of the Benares Hindu University :—

### Assay Laboratory College of Mining & Metallurgy.

Stands, Burners, Glass and Porcelain ware, etc.

1 retort stand with 2 rings.	12 test tubes.
2 tripods.	1 boiling tube.
1 funnel stand.	4 beakers-750-200 ml. capacity.
2 burette clamps.	4 cover glasses 5" to 2½"
1 test tube stand	1 wash bottle 500 ml. capacity.
2 Bunsen burners	2 ordinary flasks 200-250-ml.
2 mush room tops	capacity,
2 lengths of rubber tubing	2 sheets of wire gauze
1 asbestos sheet 6" × 6"	3 conical flasks 500—150 ml.
1 pipe clay triangle.	capacity.
1 pair of crucible tongs	8 funnels.
1 sand bath	1 measuring flask (250 ml.)
1 test tube holder.	1 weighing bottle.
1 spatula.	1 dropping bottle.
1 camel hair brush.	2 burettes, 25 ml.
	one with stop cock.
	one with pinch cock.
1 test tube brush.	1 pipette ( 20 or 25 ml. )
1 wooden rod.	3 bottles ( each 250 ml.. )
1 earthenware flame shield	1 desiccator.
2 pieces of glass tubing 6" and 8' long.	2 glass rods 6" and 8" pieces.
1 cobalt glass 2" × 2"	1 crucible with lid.
1 evaporating basin (200 ml.)	1 casserole (800 ml.)

The following acid proof wood stain recommended on page 1511 of 'Handbook of Chemistry and Physics', 1933, has proved very serviceable as varnish for the tops of the Working-Benches :—

## Solution No. 1.

425 gms. of copper sulphate  
( 25 gms. of potassium chlorate  
1000 gms. of water.

## Solution No. 2.

140 gms. of good fresh aniline oil  
190 gms. of con. hydrochloric acid  
1000 gms. of water.

Free the top of the table from paint, varnish, grease or chemicals by sand-papering it after scraping off old paint or varnish. Apply two coats of solution No. 1, boiling hot, with a paint brush, allowing each coat to dry thoroughly before the next coat is applied. Then apply two coats of solution No. 2 in the same way. When the wood is completely dried, wash off excess of chemicals with hot soapsuds. Finish with raw linseed oil. Polish comes from rubbing the oil down with a cloth.

The reagent bottles provided on the Bench are glass-stoppered and of 250 ml. capacity except for those which are to contain Na OH solution and  $\text{Na}^2\text{CO}^3$  solution. These latter are corked. The corks are coated over with paraffin wax by dipping them in molten wax and then taking them out. The labels on the bottles are coated over with wax to prevent them from perishing by the accidental running of drops of the reagent on their surface. In the absence of printed labels, Indian ink should be used to write fresh labels. Ordinary fountain pen ink marks disappear by constant exposure to the acid fumes.

Rules, to be observed in the Assay Laboratory :—

1. Keep your Working Bench neat and clean. Always have in your cupboard a piece of cloth (bleached) about one yard square.
2. Do not throw in the sink pieces of broken test tube, crucible lid, pieces of filter paper, etc.
3. Keep your apparatus neat and clean, ready for immediate employment. Tubes used for passing  $\text{H}^2\text{S}$  into solution must be cleaned inside and out with suitable solvents.
4. Always work with as small quantities as possible in qualitative work.
5. Note down the observations in connection with your experiments as they are being performed. In quantitative work, make a note of the quantity of material taken for analysis in a pocket book. The readings of the burette, in case a volumetric method is adopted, should be noted down. If a gravimetric method is adopted, the weight of the precipitate obtained at the last step should be noted down. Enough particulars must be there in the pocketbook to enable one to make the necessary calculations.
6. Before carrying out a determination in the Laboratory, read at home the principles underlying it, the procedure, and the modification necessary when interfering elements are present. Much loss of time and waste of material and chemicals can be avoided by this procedure.
7. When an experiment cannot be completed in the course of a single day's work, the solutions and precipitates set aside must be properly labelled to avoid confusion. Glass and china marking pencils priced about Re. 1/- each are sold by Chemical Supply Houses. Their use is very convenient. Porcelain crucibles with such pencil marks have, after ignition, a red mark on them. The alteration in weight of the crucibles as a result of the change of colour of the marks is negligible.



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